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(54) Perfluoroalkyl halides and derivatives

Perfluoralkylhalogenide und Derivate

L'halogénure de perfluoroalkyle et leurs dérivés

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(56) References cited:
EP-A- 0 142 041
EP-A- 0 275 771
GB-A- 2 199 828

- JOURNAL OF FLUORINE CHEMISTRY, vol. 43, no. 2, May 1989, Lausanne, CH, pages 291 - 300; A.A. MALK et al, "Synthesis of Fluorine-Containing Nitro Compounds"
- JOURNAL OF ORGANIC CHEMISTRY, vol. 53, no. 24, 25 November 1988, Easton, US, pages 5714-5720; J.Y. BECKER et al, "Electrochemical Oxidation of Polyfluoroalkyl Iodides: Direct Anodic Transformation of C8F17CH2CH2I to Amides Esters and Ethers"

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Description

This invention relates to perfluoroalkyl halides and derivatives thereof, and the preparation and use of such halides and derivatives.

Fluorocarbon derivatives (sometimes called organofluorine compounds or fluorochemicals) are a class of substances containing portions which are fluorocarbon in nature, e.g. hydrophobic, oleophobic, and chemically inert, and portions which are organic or hydrocarbon in nature, e.g. chemically reactive in organic reactions. The class includes some substances which are familiar to the general public, such as those which give oil and water repellency and stain and soil resistance to textiles, e.g. Scotchgard™ carpet protector. Other substances of the class have various industrial uses, such as reducing the surface tension of liquids, reducing evaporation and flammability of volatile organic liquids, and improving the leveling of organic polymer coatings. Examples of industrial substances are the Fluorad™ fluorochemical surfactants described in 3M Company trade bulletin 98-0211-2213-4 (38.3) BPH, issued March, 1988.

Conventional fluorochemicals can be prepared from precursors such as fluoroalkyl iodides, fluoroalkyl carboxylic acid fluorides, and fluoroalkyl sulfonyl fluorides. See for example, "Organofluorine Chemicals and Their Industrial Applications", R. E. Banks, Ed., Ellis Horwood, Ltd., Chichester, England, 1979, pp. 214-234.

Some perfluoroalkyl iodides can be prepared by telomerization of C_2F_5I or $(CF_3)_2CFI$ with C_2F_4 yielding $C_2F_5(C_2F_4)_nI$ or $(CF_3)_2CF(CF_2CF_2)_nI$, respectively, where n is typically from 1 to 4. See R. E. Banks, supra. All of the perfluoroalkyl iodides obtained from $(CF_3)_2CFI$ contain perfluoroalkyl groups with a terminal branch, and such branched-chain perfluoroalkyl groups will hereinafter be represented by "R_{fb}". All of the perfluoroalkyl iodides obtained from C_2F_5I contain straight-chain perfluoroalkyl groups without branches, and such straight-chain (or "linear") perfluoroalkyl groups will hereinafter be represented by "R_{fs}". For brevity, "R_f" will hereinafter be used to represent a perfluoroalkyl group with either a straight or a branched-chain. Perfluoroalkyl iodides can be converted into other functional (or reactive) materials, for example by the following illustrative schemes.

$$R_f\text{-}I + CH_2{=}CH_2 \rightarrow R_f\text{-}CH_2CH_2\text{-}I$$

$$R_f\text{-}CH_2CH_2\text{-}I + H_2O \rightarrow R_f\text{-}CH_2CH_2\text{-}OH$$

$$R_f\text{-}CH_2CH_2\text{-}I + H_2NC(S)NH_2 \rightarrow R_f\text{-}CH_2CH_2\text{-}SH$$

$$R_f\text{-}CH_2CH_2\text{-}I \rightarrow R_f\text{-}CH{=}CH_2$$

The alcohol, thiol, and olefin derivatives of the above schemes can be further converted to a great variety of derivatives, e.g., acrylates and polymers thereof, sulfates and salts thereof, carboxylic acids and esters thereof, etc. These further derivatives retain the original structure of the R_f, group, that is the R_f group remains either straight or branched.

Functional materials derived from telomer iodides will (as stated above) contain either 100% straight-chain (R_{fs}) or 100% branched-chain (R_{fb}) perfluoroalkyl groups. Contradictory data have been reported in the literature regarding the relative advantage of straight-chain versus branched-chain perfluoroalkyl groups. In U.S. Pat. No. 4,127,711 (Lore et al.) perfluoroalkyl straight-chains are said to be preferred for textile applications, whereas in U.S. Pat. No. 3,525,758 (Katsushima et al.) it is disclosed that surfactants containing 100% branched-chain perfluoroalkyl groups are more effective than surfactants containing straight-chain perfluoroalkyl groups in lowering the surface tension of aqueous solutions. However, it has generally been accepted that among fluorinated surfactants of the same carbon number, straight-chain products generally give lower surface tension in aqueous solutions. Banks, supra at 222-223, describes that, except at very low concentrations (less than 0.01% or 100 ppm), lower surface tension is attained with straight-chain fluorochemicals. Additionally, an article written by Bennett and Zismann (J. Phys. Chem., 71, 1967, p. 2075-2082) discloses that a condensed monolayer of a fully fluorinated straight-chain alkanoic acid has a lower critical surface energy than its terminally branched analogue with the same chain length.

In addition to the telomerization procedure described above, another method of producing many fluorochemicals or their precursors is the fluorination process commercialized initially in the 1950s by 3M Company, which comprises passing an electric current through a mixture of the organic starting compound and liquid anhydrous hydrogen fluoride. This fluorination process is commonly referred to as "electrochemical fluorination" or "ECF". Some early patents describing such technology include U.S. Pat. Nos. 2,519,983 (Simons), 2,567,011 (Diesslin et al.), 2,666,797 (Husted et al.), 2,691,043 (Husted et al.), and 2,732,398 (Brice et al.); they describe the preparation of such fluorochemical compounds as perfluoroalkyl carbonyl fluorides, e.g. $C_4F_9\text{-}COF$, and perfluoroalkyl sulfonyl fluorides, e.g. $C_4F_9\text{-}SO_2F$, and derivatives thereof.

When perfluoroalkyl carbonyl fluorides and perfluoroalkyl sulfonyl fluorides are prepared by electrochemical fluorination (ECF) of appropriate hydrocarbon precursors, the resulting products are mixtures of compounds, where some of said compounds contain a straight-chain perfluoroalkyl group, e.g., $R_{fs}\text{-}SO_2F$, and others of said compounds contain a branched-chain perfluoroalkyl group, e.g., $R_{fb}\text{-}SO_2F$. Such mixtures of compounds result even when the starting mate-

rials contain only compounds with straight-chain alkyl groups. Such mixtures of compounds, e.g. a mixture of R_{fs}-SO_2F and R_{fb}-SO_2F, can be represented, for brevity, by the formula, $R_{fsb}SO_2F$, which formula represents a mixture of compounds. The "sb" subscripts indicate that the formula represents a mixture of compounds, that is, a mixture of R_{fs}-SO_2F and R_{fb}-SO_2F.

ECF-derived acid fluorides can be converted into other functional materials, for example by the following illustrative schemes.

R_{fsb}-COF → R_{fsb}-CH_2-OH	dihydro derivatives
R_{fsb}-COF → R_{fsb}-CON(R)CH_2CH_2-OH	carboxamido derivatives
R_{fsb}-SO_2F → R_{fsb}-SO_2N(R)CH_2CH_2-OH	sulfonamido derivatives

Each R_{fsb} containing formula, e.g., R_{fsb}-COF, represents ECF derived mixtures which contain some compounds with a straight-chain perfluoroalkyl group and other compounds with a branched-chain perfluoroalkyl group.

U.S. Patent No. 2,950,317 (Brown et al) describes a process for the preparation of fluorocarbon sulfonyl chlorides from the corresponding fluorocarbon sulfonyl fluorides.

An article by Park et al. (23, J. Org. Chem, 1166-1169 (1958)) describes the preparation of certain fluorochemical compounds with three or less fully-fluorinated carbon atoms. Compounds described include n-C_3F_7-CH_2CH_2-I and n-C_3F_7-CH_2-CO_2H.

Briefly, the present invention, in one aspect, provides a fluorochemical composition comprising a mixture of compounds wherein said mixture comprises compounds of the general formula R_{fs}-$CH_2CH(R^1)$-R^2-X and compounds of the general formula R_{fb}-$CH_2CH(R^1)$-R^2-X; wherein R_{fs}- is a straight-chain perfluoroalkyl group and R_{fb}- is a branched-chain perfluoroalkyl group; - $CH_2CH(R^1)$-R^2- is a fluorine-free alkylene linking group where R^1 is selected from H a lower organic moiety of 1 to 4 carbon atoms, a phenyl group, and combinations of said lower organic moiety and said phenyl group provided that R^1 may also contain heteroatoms, and wherein R^2 is selected from a covalent bond, an alkylene group of 0 to 20 carbon atoms, and -CH(R)- where R is as defined for R^1 provided that R^2 may also contain heteroatoms; and x is a halogen atom selected from Cl, Br and I; and wherein in from 50 to 95% of said compounds the perfluoroalkyl group is straight-chain and in all others of said compound said perfluoroalkyl group is branched-chain.

As mentioned, some of said perfluoroalkyl halide compounds of said mixture contain a straight-chain perfluoroalkyl group, e.g., $CF_3CF_2CF_2CF_2$-, and some contain a branched-chain perfluoroalkyl group, e.g., $(CF_3)_2CFCF_2$-. Said perfluoroalkyl halide compounds comprise a perfluoroalkyl group, a halogen atom selected from the group consisting of Cl, Br, and I, and a fluorine-free alkylene linking group bonded to said perfluoroalkyl group and to said halogen atom. Said alkylene linking group contains at least two catenary carbon atoms one of which is bonded to said perfluoroalkyl group and the other carbon atom being bonded to said halogen atom, e.g. as in R_{fsb}-CH_2CH_2-I, but not as in R_{fsb}-$CH(CH_3)$-I. The carbon atom of the alkylene linking group which is directly bonded to said perfluoroalkyl group will be referred to as the alpha carbon atom, and the catenary carbon atom of the alkylene linking group which is bonded to said alpha carbon atom will be referred to as the "beta carbon atom". Such α and β carbon atoms are illustrated, for example, in the formula

$$R_{fsb}-\underset{\alpha}{CH_2}-\underset{\beta}{CH_2}-I$$

(The term "straight-chain" is used herein in its accepted sense to mean normal or unbranched.)

In another aspect, this invention provides novel fluorochemical compositions which comprise a mixture of perfluoroalkyl derivative compounds of said perfluoroalkyl halide compounds. Some of said perfluoroalkyl derivative compounds of said mixture contain a straight-chain perfluoroalkyl group, e.g., $CF_3CF_2CF_2CF_2$-, and some contain a branched-chain perfluoroalkyl group, e.g., $(CF_3)_2CFCF_2$-. Said derivatives are obtained from said halides by one or more steps, and retain from the precursor halides the perfluoroalkyl group and the alpha and beta carbon atoms of the linking group. One or both of said alpha and beta carbon atoms may be converted for example, to a carbonyl (C=O) or alkenylene carbon atom (C=C), but they are always retained in some form in the derivative.

As mentioned, the compositions of this invention comprise a mixture of compounds wherein 50 to 95% of said compounds contain a straight-chain perfluoroalkyl group (R_{fs}), and wherein 5 to 50% of said compounds contain a branched-chain perfluoroalkyl group (R_{fb}). Most preferably, the compositions of this invention comprise a mixture of compounds wherein 60 to 90% of said compounds contain a straight-chain perfluoroalkyl group (R_{fs}), and wherein 10 to 40% of said compounds contain a branched-chain perfluoroalkyl group (R_{fb}).

The compositions of this invention also may contain mixtures of compounds such that the number of carbon atoms

in the perfluoroalkyl groups are predominately, e.g., greater then 70%, of one length, for example where greater then 70% of all perfluoroalkyl groups in the mixture of compounds have 8 carbon atoms.

Because of the wide variety of the fluorochemical compositions of this invention, they can be used in numerous applications, including those where conventional fluorochemicals are used. Such applications are described, for example, in Banks, supra. The fluorochemical compositions of this invention are useful in improving or imparting properties to solutions and substrates such as wetting, penetration, spreading, leveling, foaming, foam stabilization, flow properties, emulsification, dispersability, and oil, water, and soil repellency.

A class of the fluorochemical compositions of this invention comprises a mixture of perfluoroalkyl halide compounds which mixture can be represented by Formula I.

$$R_{fsb}\text{-}CH_2CH(R^1)R^2\text{-}X \qquad \text{I.}$$

In Formula I, the "fsb" subscript is meant to indicate that Formula I represents a mixture of compounds, that is, a mixture of R_{fs}-$CH_2CH(R^1)R^2$-X and R_{fb}-$CH_2CH(R^1)R^2$-X. Some of said compounds contain a straight-chain perfluoroalkyl group (R_{fs}) and all others of said compounds contain a branched-chain perfluoroalkyl group (R_{fb}).

In Formula I, R_{fsb} is a perfluoroalkyl group. Said perfluoroalkyl group is saturated, mono-valent, and has at least 4 fully-fluorinated carbon atoms. While the perfluoroalkyl group can contain a large number of carbon atoms, compounds where the perfluoroalkyl group is not more than 20 carbon atoms will be adequate and preferred since larger radicals usually represent a less efficient utilization of the fluorine (lower fluorine efficiency) than is obtained with shorter chains. Perfluoroalkyl groups containing from about 4 to about 10 carbon atoms are most preferred.

In Formula I, R^1 is a lower alkyl group, with 1 to 4 carbon atoms, or a phenyl group, or combinations thereof, e.g. tolyl. R^1 may also contain hereto atoms, e.g., S, O, N, Si, for example R^1 may be $-CH_2$-OH.

In Formula I, R^2 is a covalent bond or an alkylene group such as $(CH_2)_m$, where m is from 1 to 20, or -CH(R) where R is as defined for R^1, and R^2 may also contain said hereto atoms.

In Formula I, the carbon atom bonded to the perfluoroalkyl group may be referred to as the alpha carbon atom and is represented in Formula I as the "C" in CH_2. The other depicted carbon atom, which is bonded to the alpha carbon atom, may be referred to as the beta carbon atom and is represented in Formula I as the "C" in $CH(R^1)$.

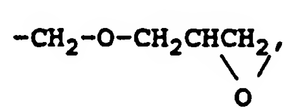
In Formula I, X is I, Cl, or Br.

A subclass of the fluorochemical compositions of this invention comprises a mixture of perfluoroalkyl halide compounds which mixture can be represented by Formula II.

$$R_{fsb}\text{-}(CH_2CH_2)_n\text{-}X \qquad \text{II}$$

In Formula II, R_{fsb} and X are as described above for Formula I and n is an integer from 1 to 5.

The perfluoroalkyl halide mixtures of this invention are reactive chemicals and can be converted into their reactive or functional derivatives by one or more steps. A class of such derivatives can be represented by the formula R_{fsb}-Z where R_{fsb} is as defined and described above and Z is an organic moiety or an oxygen-containing inorganic moiety that is a one-step or multi-step derivative of the halide compounds. Various functional embodiments of Z make the derivatives useful reagents for the introduction of the R_{fsb} moiety into molecules. Z can be an organic functional moiety, i.e., one which contains one or more carbon atoms, such as carbonyl-containing, sulfonyl-containing, alkylene-containing, nitrogen-containing, and oxygen-containing moieties or Z can be an oxygen-containing inorganic moiety, such as sulfonyl-containing and sulfonyloxy-containing moieties. Representative functional Z moieties are, for example, polymerizable groups which will undergo electrophilic, nucleophilic, or free radical reaction, derivatives with such groups being useful to form polymers comprising polymeric chains having a plurality of pendant perfluroalkyl groups. Derivative compounds of this invention include carboxylic and sulfonic acids and their metal and ammonium salts, esters, including alkyl and alkenyl esters, amides, tetrahydroalcohols ($-C_2H_4OH$), esters of tetrahydro-alcohols, acrylates (and polyacrylates), mercaptans, alkenyl ethers, etc. Stated otherwise, Z in the above formulas can contain -COOH, $-COOM_{1/v}$, $-COONH_4$, $-CH_2COOR$, $-CONH_2$, $-COONR^1R^2$, $-NR^1R^2$, $-CONR^1R^3A$, $-CH_2OH$,



$-CF_2OCF(CF_3)COF$, $-CH_2NCO$, $-CH_2SH$, -CN, $-SO_3H$, $-SO_3M_{1/v}$, $-SO_3NH_4$, $-SO_2NR^1R^2$, $-SO_2NR^1R^3A$, $-SO_2NH_2$, $-SO_3R$, $-CH_2SH$, $-CH_2NR^1R^2$, $-CH_2OCOCR^4{=}CH_2$, $CH_2OCOCF_2SF_5$, and the like, where M is a metal atom having a valence "v", such as a monovalent metal atom like K or Na; R is alkyl (e.g. with 1 to 14 carbon atoms), aryl (e.g. with 6 to 10 or 12 ring carbon atoms), or a combination thereof (e.g. alkaryl or aralkyl); R^1 and R^2 are each independently H

or R; R^3 is alkylene (e.g. with 1 to 13 carbon atoms; R^4 is H or CH_3; A is an aliphatic or aromatic moiety, which can contain a carboxy or sulfo group or an alkali metal or ammonium salt or ester thereof, a carboxamido, a sulfonamido, or contain 1 to 3 hydroxy groups, 1 or more ether-oxygen or oxirane-oxygen atoms, a cyano group, a phosphono group, or one or more primary, secondary, or tertiary amine groups, or quaternized amine group, or other functional group.

The above illustrated derivatives can be converted to other derivative fluorochemical compositions of this invention. For example, hydroxy functional derivatives can be converted to corresponding sulfate derivatives useful as surfactants as described, for example, in U.S. Pat. No. 2,803,656 (Ahlbrecht et al.) or phosphate derivatives useful as textile and leather treating agents as described, for example, in U.S. Pat. No. 3,094,547 (Heine). Hydroxy functional derivatives can also be reacted with isocyanates to make carbamato-containing derivatives such as urethanes, carbodiimides, biurets, allophanates, and quanidines useful in treating fibrous substrates such as textiles as described, for example, in U.S. Pat. Nos. 3,398,182 (Guenthner et al.), 4,024,178 (Landucci), 4,668,406 (Chang), 4,606,737 (Stern), and 4,540,497 (Chang et al.), respectively.

Amine functional derivatives can be converted to corresponding amine salts useful as surfactants, as described, for example, in U.S. Pat. Nos. 2,764,602 (Ahlbrecht), 2,759,019 (Brown et al.) or amphoteric surfactants as described, for example, in U.S. Pat. No. 4,484,990 (Bultman et al.). Amine functional derivative can be successively reacted to form an amphoteric surfactant as described, for example, in U.S. Pat. No. 4,359,096 (Berger) (see Table I thereof).

The polymerizable functional derivatives of this invention can be used to make polymers such as polyacrylates, polyesters, polyurethanes, polyamides, and polyvinyl ethers. Such polymers can be made by conventional step-growth, chain-growth, or graft polymerization techniques or processes. The step-growth polymers can be made, for example, from those derivatives having hydroxyl, carboxyl, isocyanato, or amino polymerizable groups. The acrylate, methacrylate, or vinyl derivatives of this invention can be used to make chain-growth polymers, such as polyacrylates. Fluorochemical ethylenically unsaturated monomers of this invention can be homopolymerized to make homopolymers, or copolymerized with copolymerizable monomers to make random, alternating, block, and graft polymers. Copolymerizable monomers which can be used include fluorine-containing and fluorine-free (or hydrocarbon) monomers, such as methyl methacrylate, ethyl acrylate, butyl acrylate, octadecylmethacrylate, acrylate and methacrylate esters of poly(oxyalkylene) polyol oligomers and polymers, e.g., poly(oxyethylene) glycol dimethacrylate, glycidyl methacrylate, ethylene, vinyl acetate, vinyl chloride, vinylidene chloride, vinylidene fluoride, acrylonitrile, vinyl chloroacetate, isoprene, chloroprene, styrene, butadiene, vinylpyridine, vinyl alkyl ethers, vinyl alkyl ketones, acrylic and methacrylic acid, 2-hydroxyethyl acrylate, N-methylolacrylamide, 2-(N,N,N-trimethylammonium)ethyl methacrylate and the like.

The polymers can be applied in the form of an aqueous or non-aqueous solution or emulsion as a coating or finish to modify the free surface energy of a substrate, e.g. a non-porous substrate such as glass, metal, plastic, and ceramic or a fibrous or porous substrate such as textile, e.g., nylon carpet fiber or polyester outerwear fabrics, leather, paper, paperboard, and wood to impart oil and water repellency thereto, as described, for example, in the Banks reference supra.

The relative amounts of various comonomers which can be used with the monomers of this invention generally will be selected empirically and will depend on the substrate to be treated, the properties desired from the fluorochemical treatment, e.g., the degree of oil and/or water repellency desired, and the mode of application to the substrate. Generally, in the case of copolymers, of the interpolymerized or repeating units in the polymer chain, 5 to 95 mole percent of such units will contain pendant perfluoroalkyl groups. The fluoroaliphatic polymers of this invention can be blended with other or known polymers, such as perfluoromethyl-terminated fluoroaliphatic vinyl polymers, and the blend used to modify surface properties, e.g. of textiles such as fabrics to provide them with improved properties such as oil and water repellancy.

Fluorochemicals of this invention which are useful as surfactants generally are those having a polar group such as $-CO_2Na$, $-SO_2NHC_3H_6N^+(CH_3)_3Cl^-$, $-SO_2N(C_2H_5)C_2H_4O(C_2H_4O)_7H$, and $-CONHC_3H_6N^+(CH_3)_2CH_2CO_2^-$, these moieties being representative of the polar groups in anionic, cationic, non-ionic, and amphoteric surfactants, respectively. The surfactants are useful in improving or imparting properties to aqueous and non-aqueous (organic) liquid systems such as wetting, penetration, spreading, leveling, foaming, foam stabilization, flow properties, emulsification, dispersability, and oil, water, and soil repellency. Said liquid system generally will comprise a liquid phase (in which the surfactant will be dissolved or dispersed) and one or more other phases selected from the group consisting of another liquid phase, a gas phase, and a phase of dispersed solids (e.g. polymer solids), and the system can be in the form of an emulsion, suspension, or foam (such as an air foam). Examples of such liquid systems, or application areas for said surfactants, include rinsing, cleaning, etching, and plating baths, floor polish emulsions, photographic processes, water base coatings, powder coatings, solvent based coatings, alkaline cleaners, fluoropolymer emulsions, soldering systems, and specialty inks, such as described, for example, in 3M Bulletin 98-0211-2213-4 (38.3) BPH.

The fluorochemicals useful as surfactants also can be incorporated into or mixed with other substances. For example, if sufficiently thermally stable, they can be incorporated into polymeric materials, such as polyamides, e.g. nylon, or polyolefins, e.g., polypropylene, which are cast, blown, extruded, or otherwise formed into shaped articles, such as films and fibers, the so-incorporated fluorochemicals modifying the properties of the shaped articles, such as the oil and water repellency of their surfaces. The fluorochemical surfactants of this invention can also be mixed with other sur-

factants, such as hydrocarbon surfactants and/or the conventional fluorochemical surfactants, e.g. those disclosed in said U.S. Pat. Nos. 2,567,011 and 2,732,398, and such mixed surfactants used to form, for example, aqueous, film-forming foams as described in U.S. Pat. No. 3,562,156 (Francen).

In the following examples, it is shown that the fluorochemical compositions of this invention impart improved properties. As shown in the working examples below, some of the compositions of this invention impart improved oil repellency to textile substrates compared to fluorochemical compositions derived from ECF and containing a sulfonamido linking group. As also shown, some of the compositions of this invention provide lower surface tension to, and have better solubility in, organic or aqueous systems compared to fluorochemical compositions obtained from telomerization (compositions where all compounds have straight-chain, or where all compounds have branched-chain perfluoroalkyl groups).

A convenient route to the perfluoroalkyl halide mixtures of this invention utilizes perfluoroalkyl sulfonyl fluorides (obtained from ECF) according to the following illustrative schemes.

$$R_{fsb}-SO_2F + Na_2SO_3 + I_2 \text{ ----> } R_{fsb}-I$$
$$R_{fsb}-I + C_2H_4 \text{ ----> } R_{fsb}-C_2H_4-I \qquad \text{A}$$

$$R_{fsb}-SO_2F \text{ ----> } R_{fsb}-SO_2Cl$$
$$R_{fsb}-SO_2Cl + C_2H_4 \text{ ----> } R_{fsb}-C_2H_4-Cl \qquad \text{B}$$

$$R_{fsb}-SO_2F \text{ ----> } R_{fsb}-SO_2Br$$
$$R_{fsb}-SO_2Br + C_2H_4 \text{ ----> } R_{fsb}-C_2H_4-Br \qquad \text{C}$$

The perfluoroalkyl halide mixtures from Schemes A, B and C are readily converted to various derivatives containing for example hydroxyl, thiol, amino, acids, acid salts, esters, etc., and adducts and derivatives thereof, e.g., urethanes, acrylates and polymers thereof, etc., using conventional synthetic procedures, many of which are described in the examples. Each perfluoroalkyl halide mixture can be converted to either of the other two perfluoroalkyl halide mixtures.

In the following examples, all of the perfluoroalkyl sulfonyl fluorides utilized in Examples of this invention were prepared from the hydrocarbon precursors by electrochemical fluorination (ECF). Also in the following Examples "(CE)" means Comparative Examples.

EXAMPLES

Example 1

In this example, the conversion of a perfluoroalkyl sulfonyl fluoride to a 1,1,2,2-tetrahydroperfluoroalkyl iodide, $R_{fsb}CH_2CH_2I$, will be described. Into a three-necked 5L flask, fitted with a reflux condenser, thermometer, and stirrer, were placed 585 g 1,4-dioxane, 585 g deionized water and 248 g sodium sulfite. Using the synthetic procedure outlined in U.S. Patent No. 3,420,877, Example 2, except 700 g perfluorodecanesulfonyl fluoride was used instead of perfluorooctanesulfonyl fluoride, and 435 g iodine instead of bromine. The perfluorodecanesulfonyl fluoride used comprised a mixture of about 65% straight-chain isomer and about 35% branched-chain isomer. After the reaction was completed, the perfluorodecyliodide formed was steam distilled out of the reaction mixture to give 428 g (72%) yellow product boiling 94°C to 100°C. The product was washed at about 45°C with a 400 g 10% sodium sulfite solution in water. The product (419 g) was a colorless liquid at 45°C and a solid-liquid mixture at room temperature. F-NMR analysis indicated that about 65% of the perfluoroalkyl chains were linear, about 10% contained a perfluorinated isopropyl branch, $-CF(CF_3)_2$ at the end of the carbon chain, about 0.2% contained a terminal perfluoro t-butyl group $-C(CF_3)_3$ and the remainder contained internal branches. The F-NMR data were obtained by using a solution of the product in acetone D6 and using a 94.2 MHz F-NMR instrument.

Into a 3 L steel kettle were placed 295 g (0.45 mole) of perfluorodecyl iodide from above, 1.8 g di t-butylperoxide and 4.6 g catalyst. The catalyst was prepared by mixing 30 g alumina, 2 g anhydrous cupric chloride, 2 g tin tetrachloride and 8 mL 2-aminoethanol. The reactants formed a blue-violet powder. The reactor was degassed and a nitrogen atmosphere was established. 12.8 g ethylene (0.45 mole) was charged into the reactor in 3 equal portions. After each addition, the pressure rose to about 120 psi (0.83 MPa) at a temperature of 108°C. In about 30 minutes after the first addition, the pressure dropped to about 40 psi (0.28 MPa) and the second portion of ethylene was added. The third por-

tion was added in similar fashion. After all the ethylene was charged, the heating was continued at 108°C until the pressure had decreased to 40 psi (0.28 MPa) and stabilized at this pressure, indicating all ethylene was consumed. The warm reaction product was drained from the reactor. A slightly yellow solid product (307 g) was obtained. H-NMR analysis indicated that the perfluorodecyl tetrahydroiodide $C_{10}F_{21}CH_2CH_2I$ was formed. The product was dissolved in 1000 g acetone, and the catalyst filtered off. After solvent evaporation, a slightly yellow solid was obtained. F-NMR analysis indicated that the perfluorinated chain composition of the perfluorodecyl tetrahydroiodide product was essentially the same as that of the perfluorodecyliodide precursor.

Examples 2-4 and Comparative Example 5

Following the procedure outlined in Example 1, the products of Examples 2 to 4 and Comparative Example 5 were prepared.

TABLE 1

Example	Starting Material (% straight-chain isomer)	End Product
2	$C_4F_9SO_2F$ (90%)	$C_4F_9CH_2CH_2I$
3	$C_6F_{13}SO_2F$ (80%)	$C_6F_{13}CH_2CH_2I$
4	$C_8F_{13}SO_2F$ (70%)	$C_8F_{17}CH_2CH_2I$
5(CE)	*$C_{10}F_{21}SO_2F$ (about 40%)	$C_{10}F_{21}CH_2CH_2I$

* Perfluorodecanesulfonyl fluoride at room temperature was a mixture of liquid components and semi-solid components. In Example 1, the semi-solid $C_{10}F_{21}SO_2F$ was used; F-NMR indicated that this fraction contains a major portion (about 65%) of linear perfluorinated chains. In Example 5, the liquid components of perfluorodecanesulfonyl fluoride (about 40% linear, 60% branched) were used. F-NMR indicated the following composition of the resulting perfluordecyltetrahydroiodide product of Example 5: about 40% linear perfluorinated chain, about 10% terminal perfluoroisopropyl group, about 3.0% terminal perfluoro t-butyl group and the remainder (about 44.5%) internally branched material, CF_3-$(CF_2)_x$-$CF(CF_3)$-$(CF_2)_y$-, where x and y are each greater than zero.

F-NMR indicated that the products of Examples 2-4 comprised a mixture of compounds with the following approximate composition: linear chains, CF_3-$(CF_2)_x$-, 70 - 90%; branched-chains 10-30% comprising perfluoroisopropyl branches, $(CF_3)_2CF(CF_2)_x$, about 10%; perfluoro t-butyl branches, $(CF_3)_3C$-$(CF_2)_x$ about 0.3%; and internal branching, about 15 to 20%.

In Examples 6-11, the conversion of perfluoroalkanesulfonyl fluorides to tetrahydrochlorides (Examples 6-10) and homologs and a tetrahydrobromide (Example 11) are described.

Example 6

Perfluorooctanesulfonyl chloride was prepared from the corresponding sulfonyl fluoride (U.S. Patent No. 3,420,877) containing about 70% straight-chain and 30% branched-chain isomers. The crude reaction product was washed with water, dilute aqueous potassium bicarbonate, water and dried with anhydrous sodium sulfate. Perfluorooctanesulfonyl chloride (12 g, 0.0232 mole) and di t-butyl peroxide (0.40 g) were added to a thick wall glass ampoule. The ampoule was placed in a liquid nitrogen bath, evacuated with a pump, then ethylene (1.28 g, 0.046 mole) was condensed into the ampoule. The ampoule was sealed, placed into a Hastalloy B vessel which had been padded with a glass wool cushion, and the vessel was pressurized with nitrogen gas (to balance the pressure inside the ampoule). The reaction vessel was heated at 115°C for 6 hours, cooled to room temperature; then the glass ampoule cooled in liquid nitrogen and opened to yield a dark brown, semi-solid product (11 g). GC/MS analysis showed the product to be a mixture of $C_8F_{17}CH_2CH_2Cl$ and $C_8F_{17}(CH_2CH_2)_2Cl$. NMR analysis showed a product ratio of 2:1 of the 1 to 1 and 1 to 2 adducts. The product contained a mixture of compounds, 70% of which contained straight-chain and 30% of which contained branched-chain perfluoroalkyl group.

Example 7

In this example, in order to better control the product ratios, ethylene was added incrementally to a heated mixture of perfluorooctanesulfonyl chloride using di t-butyl peroxide as free radical initiator. Thus a mixture of $C_8F_{17}SO_2Cl$ (300 g, 0.58 mole) and di t-butyl peroxide initiator (1.8 g) was charged into a 300 mL Monel reactor. Ethylene (2.6 g) was added, and the mixture was heated with shaking to 115°C. Additional ethylene charges (2.5, 4.0, 3.0, and 2.7 g) were incrementally added over a three hour period for a total of 14.7 g of ethylene. Upon cooling to room temperature a slushy product (303 g), mainly $C_8F_{17}C_2H_4Cl$, was obtained.

Example 8

Similarly, $C_8F_{17}SO_2Cl$ (30 g) was dissolved in isooctane (30 g), benzoyl peroxide (0.1 g) added and the mixture agitated at 100°C in a glass lined Hastalloy B reactor containing excess ethylene gas (8 g). After an eight hour reaction time at 100-105°C, the product, mainly $C_8F_{17}C_2H_4Cl$, was isolated as a light, cream-colored solid.

Example 9

A mixture of 10 g (0.024 mole) perfluorohexanesulfonyl chloride containing about 80% straight-chain isomer, ethylene (1.3 g, 0.046 mole), and di t-butyl peroxide (0.4 g) was placed in a glass ampoule. The mixture was heated at 100°C for 18 hours. The product was isolated as a dark-colored liquid. GC analysis showed a product ratio of 3:2 of 1:1 and 1:2 adducts. Mass spectral analysis and plasma chromatography showed the products contained no sulfur and had the structures $C_6F_{13}CH_2CH_2Cl$ and $C_6F_{13}(CH_2CH_2)_2Cl$.

Example 10

Perfluorodecanesulfonyl chloride prepared from the corresponding sulfonyl fluoride (about 60% straight-chain isomer), was used to prepare the corresponding tetrahydrochloride product. The perfluorodecanesulfonyl chloride (20.0 g, 0.032 mole), ethylene (5.0 g, 0.17 mole) and azobisisobutyronitrile (VAZO 64) were placed in a glass-lined 180 mL capacity Hastalloy B reactor and the vessel shaken and heated to 70-75°C for 16 hours. The reaction vessel was cooled, excess pressure released, and the product (21.3 g) isolated as a waxy solid. A sample was purified by vacuum sublimation to afford a white crystalline product. Analysis by NMR and GC/MS verified the product to be a mixture of predominantly 1:1 and 1:2 adducts having the structure $C_{10}F_{21}(CH_2CH_2)_nCl$ where n is mainly 1 and 2 with a very small amount of (<5%) product where n = 3.

Example 11

Perfluorobutanesulfonyl bromide was prepared using the method described by Harzdorf in Justus Liebig's Annalen der Chemie 1973, 33-39, whereby perfluorobutane sulfinic acid (from $C_4F_9SO_2F$ about 90% linear isomer) was brominated in acetic acid. A mixture of perfluorobutanesulfonyl bromide (10.0 g, 0.0226 moles), ethylene (0.046 moles) and di t-butyl peroxide 10.4 g) was heated at 90°C for 16 hours in a glass-lined 180 cc Hastalloy B reactor. At the end of the reaction, a dark liquid (6.5 g) was isolated. The acidic components in the reaction mixture were removed by washing the liquid phase with aqueous potassium bicarbonate solution followed by two water washes and drying with sodium sulfate. GC/MS analysis showed the presence of a low boiling component (C_4F_9Br) and the desired products $C_4F_9CH_2CH_2Br$ and $C_4F_9(CH_2CH_2)_2Br$ in a 2:3 ratio.

Example 12

In this example, the conversion of a perfluoroalkyltetrahydroiodide to a perfluoroalkyl tetrahydroalcohol will be described.

Into a 3 L, three-necked flask, fitted with a stirrer, a reflux condenser, and a thermometer, were placed 574 g (1 mole) of $C_8F_{17}CH_2CH_2I$, as prepared in Example 4, 594 g (6 moles) of N-methylpyrrolidone and 72 g (4 moles) of water. The mixture was heated to reflux (about 117°C). The reaction was continued for 40 hours to yield a dark brown reaction mixture, which was cooled to about 80°C to give a 2 phase reaction mixture. Deionized water (1 L) was added and the mixture heated to 70°C for 1 hour to give 2 liquid phases. The brown bottom phase containing the reaction product was separated and washed two additional times at about 70°C using 1 L of water each time. The bottom product phase was separated from the water layer and purified by steam distillation using a Dean Stark trap with 400 mL water. Product boiling from 94°C to 102°C was collected. Total yield was 475 g, about 40 g was liquid, the remaining 435 g a slushy solid. The liquid was identified by H-NMR and GC-MS to be the olefin, $C_8F_{17}CH=CH_2$. The solid analyzed by gas chromatography was shown to be the 95% of the tetrahydroalcohol, $C_8F_{17}CH_2CH_2OH$. The remainder was unreacted tet-

rahydroiodide. The yield of tetrahydroalcohol was 84%. F-NMR analysis indicated that the product mixture, contained about 74% linear chains, about 11% terminal perfluoroisopropyl groups, about 0.2% terminal perfluoro t-butyl groups, and about 14% internal branching. Upon standing at room temperature, the slushy solid separated into 2 physical phases: a small top liquid phase and a major bottom semi-solid phase. The top liquid was separated off and analyzed by F-NMR. The mixture of compounds of the liquid phase contained about 44% linear materials, about 12% terminal perfluoroisopropyl groups, about 0.3% terminal t-butyl groups, and about 43% internal branches.

Examples 13, 14

Using the procedure outlined in Example 12, the following perfluoroalkyl tetrahydroalcohols were made from the tetrahydroiodides of Examples 1 and 2.

TABLE 2

EXAMPLE	STARTING MATERIAL (% straight-chain)	END PRODUCT	YIELD
13	$C_4F_9CH_2CH_2I$ (90%)	$C_4F_9CH_2CH_2OH$	88%
14	$C_{10}F_{21}CH_2CH_2I$ (65%)	$C_{10}F_{21}CH_2CH_2OH$	80%

Example 15

In this example, the conversion of perfluoroalkyl tetrahydroiodide to a perfluoroalkyl tetrahydrothiol will be described.

Into a 3 L, three-necked flask, fitted with a stirrer, a thermometer, and a reflux condenser, were placed 574 g (1 mole) of perfluorooctyl tetrahydroiodide (prepared as described in Example 4), $C_8F_{17}CH_2CH_2I$, 114 g (1.5 mole) of thiourea and 400 g of ethanol. The reaction mixture was heated at 75°C under a nitrogen atmosphere for 5 hours. The reaction was cooled to 50°C under nitrogen. Then 120 g of a 50% solution of NAOH (1.5 mole) and 200 g deionized water were added and heating at 50°C continued for 1 hour. Addition of 1 L of water gave 2 liquid phases. The brown bottom phase containing the reaction product was washed twice with 1 L of water at room temperature and the product phase separated. A Dean Stark trap was set up, 400 g of water added, and the perfluoroalkyl tetrahydrothiol product steam distilled at a temperature of 94°C to 99°C, to give 430 g of a colorless liquid product. Gas chromatographic analysis indicated an 84% yield of $C_8F_{17}CH_2CH_2SH$, and about 2% olefin, $C_8F_{17}CH{=}CH_2$. F-NMR indicated that the $C_8F_{17}CH_2CH_2SH$ product mixture contained about 77% linear chains, about 9% terminal perfluoroisopropyl groups, about 0.2% terminal perfluoro t-butyl groups, and about 13% internal branching.

Examples 16-19

Using the procedure outlined in Example 15, the following perfluoroalkyl tetrahydrothiols were made:

TABLE 3

EXAMPLE	STARTING MATERIAL (% straight-chain)	END PRODUCT	YIELD
16	$C_4F_9CH_2CH_2I$ (90%)	$C_4F_9CH_2CH_2SH$	75%
17	$C_{10}F_{21}CH_2CH_2I$ (65%)	$C_{10}F_{21}CH_2CH_2SH$	88%
18(CE)	$C_{10}F_{21}CH_2CH_2I$ (40%)	$C_{10}F_{21}CH_2CH_2SH$	85%
19	$C_8F_{17}(CH_2CH_2)_{1.3}Cl$ (70%)	$C_8F_{17}(CH_2CH_2)_{1.3}SH$	33%

Example 20

In this example, the conversion of a perfluoroalkyl tetrahydroalcohol into the corresponding perfluoroalkyl acrylate is described.

Into a three-necked 500 mL flask, fitted with a condenser, a stirrer, and a thermometer, were placed 232 g (0.5 mole) of perfluorooctyl tetrahydroalcohol (prepared as described in Example 12) $C_8F_{17}CH_2CH_2OH$, and 90 g methyl ethyl ketone (MEK). Using a Dean Stark trap, 20 g MEK was distilled out, the reaction mixture cooled to room temperature under nitrogen, then 50.5 g (0.5 mole) of dry triethylamine and 100 ppm Irgonox 1010 antioxidant (Ciba-Geigy) were added. Using an addition funnel and a nitrogen purge, 45 g (0.5 mole) of acryloyl chloride were added over a 1 hour period. An exotherm of about 20°C was noticed. A white slurry was obtained in the exothermic (about 20°C temperature rise) reaction. After the addition was complete, the reaction mixture was maintained at 50°C for 2 hours. Gas chromatographic analysis indicated a conversion of 95% to acrylate. The reaction mixture was washed three times using 200 mL of water. The yield of colorless liquid product, $C_8F_{17}CH_2CH_2OCOCH{=}CH_2$, was 237 g (94%).

Example 21

Following the procedure of Example 20, $C_4F_9CH_2CH_2OCOCH{=}CH_2$, was prepared in a 90% yield as a slightly yellow liquid, starting from the alcohol of Example 13.

Example 22

In this example, the conversion of perfluoroalkyl tetrahydroiodide into a perfluoroalkyl olefin will be described.

Into a 1 L, three-necked flask, fitted with a condenser, a thermometer, and a stirrer, were placed 57.5 g (0.1 mole) perfluorooctyl tetrahydroiodide as prepared in Example 4, 100 g isopropanol and 8.4 g (0.15 mole) potassium hydroxide. The reaction mixture was heated at reflux for 5 hours to give a brown reaction mixture. Gas chromatographic analysis showed a conversion to about 96% olefin. Deionized water (400 mL) was added and the reaction mixture was steam distilled using a Dean Stark trap. In a temperature range 94-98°C, 43 g (95%) of colorless liquid olefin product, $C_8F_{17}CH{=}CH_2$, was obtained in a purity greater than 98%. F-NMR analysis indicated that the mixture of compounds contained about 74% linear material, about 10% terminal perfluoroisopropyl, about 0.2% terminal perfluoro t-butyl, and about 13% internal branching.

Comparative Example 23

Following the procedure of Example 22, $C_{10}F_{21}CH{=}CH_2$ was prepared from the tetrahydroiodide of Example 5. This olefin product mixture contained about 42% linear perfluorinated chains, about 10% perfluoroisopropyl terminated, and about 46% internally branched material.

Example 24

In this example, the conversion of a perfluoroalkyl tetrahydroalcohol into a perfluoroalkyl dihydrocarboxylic acid is described.

Into a 1 L, three-necked flask, fitted with a reflux condenser, a thermometer, and a stirrer, were placed 46.6 g (0.1 mole) of tetrahydroalcohol, $C_8F_{17}CH_2CH_2OH$ (prepared in Example 6), and 450 g acetone. The solution was cooled to about 5°C in an ice bath and 23.7 g (0.15 mole) of potassium permanganate added in small portions over a 2 hour period. The reaction was exothermic, and a color change from purple to brown was observed. After all the potassium permanganate had been added, the reaction was allowed to react for 1 hour at room temperature. The reaction was then slowly heated up to reflux temperature (about 58°C) and maintained for about 3 hours. Then 50 g of water were added to the brown product slurry and all acetone was removed by distillation. The reaction was cooled to about 5°C using an ice bath, and 100 g of 95% sulfuric acid were added slowly over a 2 hour period. After the acid addition, the reaction mixture was heated at 95°C for 2 hours. After cooling to about 40°C, 200 mL of water was added to the two-phase mixture. The brown bottom phase was separated from the water layer at 65°C and washed twice using 200 mL water at 75°C. The bottom phase was collected and distilled. The product fraction collected from 100°C to 130°C at about 20 torr yielded 35 g of a solid material at room temperature. GC-MS analysis indicated the presence of about 78% $C_8F_{17}CH_2COOH$, about 11% $C_8F_{17}CH_2COOCH_2CH_2C_8F_{17}$ (ester of the starting alcohol and the formed acid) and about 10% $C_8F_{17}COOH$. The yield of perfluorooctyl dihydrocarboxylic acid, $C_8F_{17}CH_2COOH$, was about 57%.

Example 25

Into a 500 mL three-necked flask, fitted with a reflux condenser, a thermometer, and a stirrer, were placed 61.8 g

(1 mole) boric acid, 232 g (4 moles) allyl alcohol and 120 g toluene. A Dean Stark trap was used to collect water during the azeotropic distillation. The initial white slurry present before the reaction mixture was heated became a clear solution after heating to reflux and forming 53 g of water in the azeotropic distillation. Toluene, excess allyl alcohol and triallyl borate ester product were distilled off. The triallyl borate (161 g, 89%) was obtained as a colorless, viscous liquid. Into a 500 mL three-necked flask, fitted with a reflux condenser, a thermometer, and a stirrer were placed 18.2 g (0.1 mole) of the above triallyl borate, 20 g ethyl acetate, 103.8 g (0.3 mole) C_4F_9I, prepared following Example Ia, and 0.2 g azobisisobutyronitrile (AIBN). The mixture was heated at about 40°C and degassed using aspirator vacuum and nitrogen. The reaction mixture was heated to reflux, and an additional 0.2 g of AIBN were added. Heating at reflux was continued for 15 hours under a nitrogen atmosphere, followed by addition of another 0.2 g of AIBN and refluxing for an additional 5 hours. Gas chromatographic analysis of the clear, yellow product solution indicated that about 2% of unreacted C_4F_9I was left unreacted and that the major product was $C_4F_9CH_2CH(I)CH_2OH$. After addition of 230 g of deionized water and distilling off ethyl acetate, the reaction mixture was heated at 95°C for 1 hour. The bottom yellow-brown organic layer containing the reaction product was washed twice with 200 g of water at 95°C.

Example 26

To the yellow-brown liquid product from Example 25 was added at room temperature, 24 g (0.3 mole) of a 50% aqueous sodium hydroxide solution, 100 g isopropanol and 30 g water. The reaction mixture was heated at 40°C for 2 hours, then 300 g of water were added. The brown bottom phase of the mixture, containing the reaction product, was washed twice with 200 g water. Distillation at reduced pressure gave 61.7 g (74% yield) of epoxy compound

$$C_4F_9CH_2\overset{\overset{\displaystyle O}{/\ \backslash}}{CH-CH_2},$$

in a purity of 93% as determined by GC, and H- and F-NMR analysis. A by product (3%) was $C_4F_9CH{=}CHCH_2OH$. The epoxy product mixture contained about 74% straight-chains, about 11% terminal perfluoroisopropyl branches and about 14% internal branching.

Example 27

Following the same procedure as in Examples 25 and 26,

$$C_8F_{17}CH_2\overset{\overset{\displaystyle O}{/\ \backslash}}{CH-CH_2},$$

was prepared from $C_8F_{17}I$ and triallyl borate. The intermediate product $C_8F_{17}CH_2CH(I)CH_2OH$ was not isolated.

The following Table shows the structures of the major products in the mixtures produced in Examples 1-27. Table 4 also lists the weight % of compounds containing a straight-chain perfluoroalkyl group and the weight % of compounds containing a branched-chain perfluoroalkyl group in each product mixture.

TABLE 4

Examples	Product	Percent straight and branched Perfluoroalkyl Groups	
		straight	branched
1	$C_{10}F_{21}CH_2CH_2I$	65	35
2	$C_4F_9CH_2CH_2I$	90	10
3	$C_6F_{13}CH_2CH_2I$	83	17
4	$C_8F_{17}CH_2CH_2I$	74	26
5 (CE)	$C_{10}F_{21}CH_2CH_2I$	40	60
6	$C_8F_{17}(CH_2CH_2)_{1.3}Cl$	70	30
7	$C_8F_{17}(CH_2CH_2)_1Cl$	70	30
8	$C_8F_{17}(CH_2CH_2)_1Cl$	70	30
9	$C_6F_{13}(CH_2CH_2)_{1.4}Cl$	80	20
10	$C_{10}F_{21}(CH_2CH_2)_{1.3}Cl$	60	40
11	$C_4H_9(CH_2CH_2)_{1.6}Br$	90	10
12	$C_8F_{17}CH_2CH_2OH$ *	74	26
(CE)	$C_8F_{17}CH_2CH_2OH$ **	44	56
13	$C_4F_9CH_2CH_2OH$	91	9
14	$C_{10}F_{21}CH_2CH_2OH$	63	37
15	$C_8F_{17}CH_2CH_2SH$	77	23
16	$C_4F_9CH_2CH_2SH$	89	11
17	$C_{10}F_{21}CH_2CH_2SH$	65	35
18 (CE)	$C_{10}F_{21}CH_2CH_2SH$	40	60
19	$C_8F_{17}(CH_2CH_2)_{1.3}SH$	75	25
20	$C_8F_{17}CH_2CH_2OCOCH{=}CH_2$	77	23
21	$C_4F_9CH_2CH_2OCOCH{=}CH_2$	90	10
22	$C_8F_{17}CH{=}CH_2$	74	26
23 (CE)	$C_{10}F_{21}CH{=}CH_2$	42	58

24	$C_8F_{17}CH_2COOH$	75	25
25	$C_4F_9CH_2CH(CH_2OH)I$	90	10
26	O / \\ $C_4F_9CH_2CH-CH_2$	89	11
27	O / \\ $C_8F_{17}CH_2CH-CH_2$	74	26

* Slushy Product

** Liquid Phase

Example 28

In this example, the conversion of a perfluoroalkyl tetrahydrothiol to a perfluoroalkyl melamine is described.

Into a 500 mL three-necked flask, fitted with a stirrer, a reflux condenser, and a thermometer, were placed 39.0 g (0.1 mole) hexamethoxymethyl melamine (HMMM) (available from American Cyanamid, as Aerotex 302), 192 g (0.4 mole) of perfluorooctyl tetrahydrothiol, from Example 15 and 0.34 g p-toluene sulfonic acid. The reaction mixture was slowly heated to 80°C under nitrogen. Methanol forming in the reaction caused some foaming. The temperature was slowly increased over a 2 hour period to 120°C. In this period, about 10 g of methanol was formed and trapped in a Dean Stark trap. The foam had completely collapsed. The reaction mixture was heated during 30 minutes from 120°C to 180°C under nitrogen yielding an additional 2.5 g methanol in the Dean Stark trap. Heating of the reaction mixture was continued at 180°C for 5 hours under a nitrogen atmosphere. The condensation reaction product was a yellow-brown solid at room temperature and comprises a mixture of compounds of formula $C_3N_6(CH_2OCH_3)_x(CH_2SC_2H_4C_8F_{17})_y$ where x and y have average values of about 2 and 4, respectively.

Into a 500 mL three-necked flask, fitted with a reflux condenser, a thermometer, and a stirrer, were charged 180 g solids of the above prepared condensate (from (a)) and 270 g butyl acetate. The reaction mixture was heated at 65°C to yield a clear yellow-brown solution.

Into a separate 1 L beaker were placed 18.0 g Marlowet™ 5401 emulsifier (Huls, Germany), 108 g ethyl Cellosolve™ and 720 g of deionized water and stirred and heated to about 65°C until a clear solution resulted. While stirring vigorously, the above butyl acetate solution of the fluorochemical melamine product was added to the aqueous solution at about 65°C. A preemulsion resulted, which was passed through a preheated (at 70°C) Manton-Gaulin emulsifier at about 4000 psi (27.6 MPa) pressure. A yellow-brown, nearly transparent emulsion at about 70°C resulted. The solvent was removed using a vacuum pump at about 1 to 10 torr and 50°C. A nearly transparent, aqueous dispersion resulted. The solids content was about 18%.

Comparative Example 29, Comparative Examples C1-C3

Following the same procedure as in Example 28 and Comparative Examples 29 and C1-C3 were prepared, as shown below. The Comparative Examples C2 and C3 contain straight-chain fluoroalkyl groups only. Comparative Example C1 contains a sulfonamido group directly attached to the perfluoroalkyl group.

TABLE 5

EXAMPLE	FLUOROCHEMICAL INTERMEDIATE USED	MOLAR RATIO HMMM/FC-INTERMEDIATE
29(CE)	$C_{10}F_{21}CH_2CH_2SH$ as prepared in Example 18	1:4
C1	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$ (available from 3M)	1:4
C2	$C_nF_{2n+1}CH_2CH_2SH$ with $\langle n \rangle = 10$ (available from Ciba Geigy)	1:4
C3	$C_nF_{2n+1}CH_2CH_2OH$ with $\langle n \rangle = 8$ (available from DuPont)	1:4

Example 28, and Comparative Examples 29 and C1 - C3 (containing R_{fs} groups), were used as dispersions to treat textile fabrics.

An aqueous treatment bath, which is usually a dispersion or emulsion, is prepared containing the fluorochemical compositions and other required or desired ingredients such as resins, catalysts, extenders, softeners, etc. The textile fabric is immersed in the treatment bath by a padding technique, which is well known to those skilled in the art. The saturated fabric is run through a roller to remove excess dispersion/emulsion, dried and cured in an oven for the desired temperature and time. The resulting treated fabrics are tested for oil and water repellency by test methods set forth below:

Water spray (SR) test	AATCC Test Method 22-1977
oil repellency (OR) test	AATCC Test Method 118-1975
Bundesmann test:	Deutche Industries Norm (DIN) 53-888
Dry cleaning procedure:	AATCC Test Method 7-1975
Laundering procedure:	A 230 g sample of 400 cm^2 to about 900 cm^2 of treated fabric is placed in a conventional washing machine along with a ballast sample (1.9 kg of 8 oz. fabric). Conventional detergent (46 g) is added and the washer filled to high water level with hot water (40 ± 3°C). The substrate and ballast is washed 5 times using 12 minute normal wash cycle and the substrate and ballast are dried together in a conventional clothes dryer for about 45 minutes. The dry substrate is pressed using a hand iron set at the temperature recommended for the particular fabric.

Evaluation (using the above test methods and procedures) of fabric samples treated with the compositions of Example 28 and Comparative Examples 29 and C1, C2 and C3 is given in Table V below.

A polyester/cotton 50/50 blend fabric was treated at 0.3% solids by weight on total weight of the fabric using a treatment bath containing: a) the fluorochemical melamine dispersions containing approximately 18 wt.% solids, as described above; b) 12 g/L resin LYOFIX CHN (Chem. Fabrik Pfersee, Germany) 6 g/L Knittex catalyst 20 (Chem. Fabrik Pfersee) and 2 mL/L acetic acid (60%). The treated fabrics were dried and cured at 150°C for 5 minutes. Results are shown in Table 6.

TABLE 6

			Bundesman			After 5 Launderings		After 1 Dry Cleaning	
	Initial		1	5	10				
			(Minutes)						
Example	OR	SR				OR	SR	OR	SR
28	6	100	5	5	5	5	90	5	100
29(CE)	5	100	5	5	5	4	90	5	90
C1	3	100	4.5	4.5	4	2	90	2	100
C2*	5	100	5	5	5	3	90	4	100
C3	5	100	4.5	3.5	3	4	80	4	90

* In the emulsification step, hexafluoroxylene was used as the organic solvent.

As the results indicate (compare, for example the results for Example 28 to the results for Comparative Examples C1 and C3) the compositions of the invention impart better oil and water repellency to fabrics, and the treated fabrics retain repellency after laundering and dry cleaning. The results show that the compositions obtained from reactions using intermediates of the invention are, at equal carbon atom content in the perfluoroalkyl group, superior to compositions made using intermediates containing 100% straight-chain perfluoroalkyl groups (R_{fs}), or compositions with a sulfonamido linking group (containing straight and branched-chain perfluoroalkyl groups). These intermediates of this invention are more effective oil and water repellency agents than those derived from the two other classes of intermediates. Even more surprising is the comparison of Example 28 and Comparative Example C2, which shows that the C_8 thiol of this invention gives a product with equal or slightly better properties than the composition derived from a straight-chain C_{10} thiol, indicating a better fluorine efficiency.

Another advantage of these intermediates and compositions of this invention is their superior solubility in organic solvents, which is important if the compositions are used as aqueous dispersions. Comparative Example C2 could only be emulsified when hexafluoroxylene was used as a solvent, while the products of Example 28 and Comparative Example 29 were easily soluble in a variety of organic solvents such as esters or ketones. The solubility of the product of Comparative Example C3 was also poorer than products of Example 28 and Comparative Example 29, although better than Comparative Example C2 (perhaps due to its shorter average chain length).

Example 30

Into a 500 mL three-necked flask, fitted with a stirrer, a reflux condenser, and a thermometer, were placed 46.4 g (0.1 mole) of $C_8F_{17}CH_2CH_2OH$ (as prepared in Example 12) and 80 g ethyl acetate. A Dean Stark trap was set up and 20 g ethyl acetate distilled out. The reaction was cooled to about 40°C under nitrogen; then 40.8 g (0.3 isocyanate equivalent) of PAPI (an oligomeric aromatic isocyanate of chemical structure:

$OCNC_6H_4CH_2[C_6H_3(NCO)]_nCH_2C_6H_4NCO$ (average of n=0.7) available from Upjohn Co.) and 3 drops of dibutyltin dilaurate were added. The reaction was heated to reflux (about 78°C) under nitrogen, and heating continued for 5 hours at reflux. The reaction mixture was cooled to about 45°C under N_2, then 17.4 g (0.2 mole) of 2-butanone oxime (Servo Comp., The Netherlands) added over about 30 minutes resulting in an immediate exotherm of about 10°C. Heating of the reaction mixture was continued for 1 hour at 60°C, after which time no isocyanate absorption by infrared analysis could be detected. A clear, brown solution containing a fluorochemical oligomeric urethane was obtained.

Into a 500 mL three-necked flask, fitted with a stirrer, a thermometer, and a reflux condenser, were placed the above obtained ethyl acetate solution and 80 g of additional ethyl acetate. The mixture was heated to about 60°C to yield a clear, brown solution. Into a separate 1 L beaker were placed 10.3 g Marlowet™ 5401 emulsifier (commercially available from Hüls), 60 g ethylene glycol and 355 g deionized water. This solution was heated to about 60°C; then under vigorous stirring, the organic solution was added to the aqueous solution. The resulting preemulsion was passed 3 times through a preheated Manton Gaulin emulsifier at about 55°C and 4000 psi (27.6 MPa) pressure. The ethyl acetate solvent was distilled out using an aspirator vacuum to yield a pale brown, slightly transparent aqueous dispersion containing about 18 wt. fluorochemical urethane oligomer.

Comparative Examples C4, C5

Using the same synthetic and emulsification procedure as in Example 30, further examples were prepared as shown in Table VI. Comparative Example C4 was made using N-methylperfluorooctanesulfonamido ethanol, $C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$, (available from 3M Company) and Comparative Example C5 was made using perfluorodecyl tetrahydroalcohol, $C_{10}F_{21}CH_2CH_2OH$ (available from Hoescht Co., Germany), double the amount of solvent had to be used during emulsification.

Using the same fabric, treatment method and test procedures as described above for Examples 28, 29, and Comparative Examples C1-C3, the following test results were obtained:

TABLE 7

Treatment with Composition of Example	Initial		5 Launderings		1 Dry Cleaning	
	OR	SR	OR	SR	OR	SR
30	4	100	3	80	2	80
C4	2	100	0	70	0	70
C5	3	100	2	80	2	70

The results indicate again that the compositions of this invention are superior to compositions containing 100% straight-chain perfluoroalkyl group. The compositions of this invention are also superior to sulfonamido derived compositions. Again, the intermediates of this invention show better fluorine efficiency, better performance and better solubility.

Example 31

In this example, compositions of the invention were used to make an oligomeric fluorochemical urethane derivative.

Into a 500 mL three-necked flask was placed 51.8 g (0.1 mole) of the acrylate prepared in Example 20, 2 g (0.025 mole) of 2-mercaptoethanol, 0.4 g AIBN initiator and 40 g ethyl acetate. The mixture was heated to about 40°C and degassed. The reaction mixture was then heated at reflux (about 78°C) for 16 hours under nitrogen. A clear, pale yellow solution was obtained, containing a hydroxy functionalized fluorochemical oligomer of average molecular weight about 2,200. Gas chromatography indicated that virtually all reagents had been reacted. The reaction mixture was cooled to about 45°C under nitrogen and about 60 g ethyl acetate was added. A Dean Stark trap was set up and 20 g ethyl acetate distilled out. The reaction mixture was cooled to about 45°C under nitrogen; then 10.2 g (0.075 isocyanate equivalents) of PAPI were added together with three drops of dibutyltindilaurate. The reaction mixture was heated at reflux (about 78°C) under nitrogen for 5 hours, then cooled to about 50°C under nitrogen. After addition of 4.3 g 2-butanone oxime (0.05 mole), the reaction mixture was heated at 70°C for 1 hour. A clear, brown solution was obtained, which was free of isocyanate groups (infrared analysis).

The oligomeric fluorochemical urethane product was emulsified and tested according to the procedures described and used for Example 30. Two commercially available fluorochemical agents were also evaluated. The fabric used was 100% cotton. The results are shown in Table 8.

TABLE 8

Treatment with Composition of Example	Initial		5 Launderings		1 Dry Cleaning	
	OR	SR	OR	SR	OR	SR
31	6	100	5	90	5	100
AG-310*	2	100	1	60	2	70
Oleophobol PF**	5	100	2	90	3	100

* AG-310 is a fluorochemical containing commercial product available from Asahi Glass Co., Ltd.

** Oleophobol PF is a fluorochemical containing product available from Chemische Fabrik Pfersee.

As can be seen, Examples of the invention give excellent results, compared to commercially available products, even on fabrics which are known to those skilled in the art to be difficult to treat.

Example 32

In this example, a fluorochemical thiol of the invention was added across the triple bond of propargyl alcohol and the resulting adduct converted into a blocked oligomeric urethane derivative. Into a 500 mL three-necked flask, fitted with a reflux condenser, a thermometer, and a stirrer, were placed 48 g (0.1 mole) of $C_8F_{17}CH_2CH_2SH$ as prepared in Example 15, 2.8 g (0.05 mole) of propargyl alcohol, 20 g methyl ethyl ketone and 0.15 g AIBN. The reaction mixture was degassed and heated at reflux (about 76°C) under nitrogen. After 6 hours, another 0.15 g AIBN was added, and the reaction continued for 15 hours at reflux under nitrogen to yield a clear, yellow solution. Gas chromatography indicated about 10% residual fluorochemical thiol. The reaction mixture was cooled to about 40°C under nitrogen; then 40 g methyl ethyl ketone, 20.4 g (0.15 isocyanate equivalents) of PAPI and three drops of dibutyltindilaurate were added. The reaction mixture was heated at reflux under nitrogen for 5 hours. The reaction mixture was cooled again to about 50°C under nitrogen; then 8.2 (0.01 mole) of 2-butanone oxime was added, and the reaction mixture heated at 70°C for 1 hour to yield a clear brown solution containing an oligomeric urethane derivative having blocked isocyanate groups and one hydroxy functionalized adduct of the fluorochemical thiols of this invention. The reactions are shown in the following scheme: (See U.S. Pat. No. 4,158,672, Ex. 1)

$$C_8F_{17}CH_2CH_2SH + HC{\equiv}C\text{-}CH_2OH \dashrightarrow (R_fCH_2CH_2S)_n\text{-}C_2H_xCH_2OH$$

$$n = 0,1,2 \quad x = 1,2,3 \quad n + x = 3$$

$$\xrightarrow[\text{2-butanone oxine}]{\text{PAPI}} \text{Oligomeric Urethane}$$

The product was emulsified following the procedure outlined in Example 30. Further compositions (Examples 33 and 34) using this procedure and emulsification procedure were prepared and are shown in Table 9.

TABLE 9

EX.	FC INTERMEDIATE A	FUNCTIONAL ALKYNE B	ISOCYANATE C	EQUIVALENTS RATIO A/B/C/2- BUTANONE OXIME
33	Example 15	2,4-hexadiyne 1,6-diol	TDI*	4/1/2/1
34	Example 15	2,4-hexadiyne-1,ol	PAPI	4/1/3/2

* Toluene Diisocyanate

The fluorochemical oligomeric urethane materials of Examples 33 and 34 were used to treat a polyester/cotton 65/35 blend fabric at 0.3% by weight of fluorochemical on fabric by the methods described above. Test results are shown in Table 10.

TABLE 10

Treatment with Composition of Example	Initial		5 Launderings		1 Dry Cleaning	
	OR	SR	OR	SR	OR	SR
32	6	100	4	90	4	90
33	3	90	1	50	2	70
34	7	100	6	80	5	80

As can be seen from the data, excellent results were obtained using the fluorochemical compositions of this invention.

Example 35

Into a carefully dried 500 mL three-necked flask, fitted with a condenser, stirrer, and thermometer, were placed 15.3 g (0.1 mole) of $POCl_3$ (under nitrogen) and 20 g toluene. Deionized water (1.8 g, 0.1 mole) was added dropwise under vigorous stirring over about 15 minutes. An exotherm of about 25°C was observed and HCl was liberated. The reaction was heated to 70°C until no more HCl was liberated. Then 46.4 g (0.1 mole) of $C_8F_{17}CH_2CH_2OH$, as prepared in Example 12, was added over 15 minutes. The reaction mixture was heated at 90°C under a gentle nitrogen flow until no more HCl was liberated (about 3 hours). The reaction was cooled to 50°C under nitrogen; then 1.8 g (0.1 mole) of deionized water was added. The reaction mixture was heated to 90°C under a gentle N_2 flow until no more HCl was liberated (about 2 hours). Then a gentle vacuum (by aspirator) was used to remove the last traces of HC1. Deionized water (200 g) was then added and all the toluene was distilled off. The reaction mixture was neutralized to pH of 8 using 10% aqueous NH_4OH and then diluted to 10% solids with isopropanol and water. (Final ratio of water/isopropanol was 70/30.) A sample of the resulting clear solution was analyzed by gas chromatography (after reacting with diazomethane) and was shown to contain approximately 3% unreacted alcohol, 85% monoester, 10% diester, and 2% triester.

The materials of the invention were diluted in water to 0.05% (500 ppm) and/or 0.01% (100 ppm), and the surface tension of the aqueous solution was measured using a Du Nouy tensiometer. Foam height was measured as volume in a graduated cylinder. Half-life time (t 1/2) is the time for half the liquid present in the foam to drain from the foam. The foam was generated by a wire wisk in a Hobart mixer. Thus, 200 mL of surfactant solution to be tested is placed in a

bowl of Hobart Model N-50 mixer equipped with a wire wisk stirrer and stirred for 3 minutes at medium speed (setting 2 = 300 rpm). The foam produced was immediately transferred to a 4000 mL graduated cylinder for measuring foam height and half-life time.

Examples 37-38, Comparative Examples 36, 39 and C6-C11

Using the synthetic procedure of Example 35, further examples (37-38) and Comparative Examples 36, 39 and C6-C11 were prepared as shown in Table 11.

TABLE 11

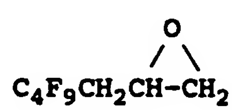
Example	Fluorochemical Alcohol Used
36(CE)	$C_8F_{17}CH_2CH_2OH$ from Example 12, containing 44% linear material
37	$C_4F_9CH_2CH_2OH$ from Example 13
38**	$C_{10}F_{21}CH_2CH_2OH$ from Example 14, containing 65% linear material
39(CE)	$C_{10}F_{21}CH_2CH_2OH$ containing 40% linear material
C6	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OH$ N-ethyl perfluorooctane-sulfonamido ethanol (available from 3M)
C7**	$C_nF_{2n+1}CH_2CH_2OH$ (n)= 8 (available from DuPont)
C8*	$C_{10}F_{21}CH_2CH_2OH$ (available from Hoechst)
C9	Zonyl FSP (ammonium salt of a fluorochemical phosphate mixture, available from DuPont)
C10	Isomers of C_6F_{11}-$CF_2OCF(CF_3)CH_2OH$ as described in EP 314,380
C11	$CF_3(CF_2)_3OCF(CF_3)CF_2OCF(CF_3)CH_2OH$

* The ammonium salts of the phosphate esters were insoluble in water/isopropanol mixtures, even at very low concentrations.

** The reaction products had to be diluted to 5% solids in water/isopropanol prior to testing.

Example 40

Into a 500 mL three-necked flask fitted with a stirrer, a reflux condenser, and a thermometer, were placed 27.6 g (0.1 mole) of



(as prepared in Example 26, 26.4 g (0.1 mole) of $C_4F_9CH_2CH_2OH$ (as prepared in Example 13) and 60 g benzene. Using a Dean Stark trap, 20 g benzene was distilled out. The reaction was cooled to about 40°C under N_2, and then 0.25 g of boron trifluoride-etherate complex in ether was added. An immediate exotherm was observed of about 10°C. The reaction was heated at 75°C under nitrogen for 5 hours, during which time a clear brown solution was formed. At room temperature, two liquid phases were obtained. The benzene layer containing the products was removed. The reaction mixture was analyzed by gas chromatography and found to contain about 15% unreacted $C_4F_9CH_2CH_2OH$ alcohol, about 70% monoadduct of 1 mole alcohol reacted with 1 mole epoxide, about 10% of diadduct of 1 mole alcohol reacted with 2 moles epoxide and about 3% of higher homologues. The reaction product was converted into a mixture of phosphate esters and their ammonium salts following the procedure described in Example 35.

Example 41

Following the procedure outlined in Example 25, the reaction product of 2 moles $C_4F_9CH_2CH_2SH$, as prepared in Example 16, and 1 mole of propargylalcohol, $CH{\equiv}CCH_2OH$, was prepared. The resulting adduct containing hydroxyl functionality was converted into the mixture of phosphate esters and their ammonium salts following the procedure

described in Example 35.

Example 42

Into a 500 mL three-necked flask, fitted with a stirrer, a reflux condenser, and a thermometer were placed 6.7 g malic acid (0.05 mole), 26.4 g (0.1 mole) $C_4F_9CH_2CH_2OH$ as prepared in Example 13), 30 g methylisobutylketone and 0.2 g p-toluenesulfonic acid. The mixture was heated at reflux (about 98°C) and H_2O was collected in a Dean Stark trap. After 6 hours of reflux, 1.7 g H_2O were trapped and the reaction stopped. All reaction solvent was removed. A diester alcohol of structure $C_4F_9CH_2CH_2OC(O)CH_2CH(OH)C(O)OCH_2CH_2C_4F_9$ was formed, which was subjected to the synthetic procedure followed in Example 35 to make ammonium salts of phosphate esters.

TABLE 12

PRODUCT OF EXAMPLE	FOAM HEIGHT (VOLUME) 500 ppm	HALF-LIFE TIME (SEC) 500 ppm	SURFACE TENSION (dyne/cm)	
			500 ppm	500 ppm
35	200	< 30 sec.	17.5	18.1
36(CE)	400	< 30 sec.	18.5	25.7
37	400	< 30 sec.	33.3	44.9
38	400	< 30 sec.	16.4	18.9
39(CE)	400	< 30 sec.	18.7	24.3
40	1100	1 min. 15 sec.	21.2	29.3
41	1000	50 sec.	21.7	36.7
42	200	< 30 sec.	21.3	28.5
C6	1600	4 min 10 sec.	17.2	18.5
C7	200	< 30 sec.	17.6	26.0
C8	insoluble			
C9	300	< 30 sec.	18.0	26.6
C10	400	< 30 sec.	20.4	26.8
C11	300	< 30 sec.	29.5	35.8

The data shows that the surfactants of this invention (compare, for example, Example 35 to Comparative Examples C6 and C7) have unexpected properties: low foaming and low surface tension in water. Compared to sulfonamido linking group containing derivatives (Comparative Example 6) our materials are low foaming, and compared to straight-chain derivatives (Comparative Example C7), the materials of this invention give lower surface tensions at equal perfluorinated chain lengths. The solubility of materials of this invention in aqueous systems is much better than their straight-chain analogues (compare Example 39 to Comparative Example C8). Compositions with 100% straight-chain materials give good properties but are usually poorly soluble at perfluorinated chain length of 8 carbons or more, and compositions with 100% branched-chain materials (Comparative Example 10 and 11) are very soluble even at long carbon chains, e.g. C_{10} or higher, but they are not as good for imparting lower surface tension. As Examples 35, 37 and 38 show, the compositions of the invention contain from 50% to 95% straight perfluoroalkyl chains and more preferably contain from 50% to 85% straight-chain linear materials (15%-50% branched).

Example 43

Into a carefully dried 500 mL three-necked flask, fitted with a reflux condenser, thermometer, and a stirrer, were placed 46.4 g (0.1 mole) of $C_8F_{17}CH_2CH_2OH$ (as prepared in Example 12) and 20 g dry dioxane under nitrogen at room temperature. Then, 0.1 mole chlorosulfonic acid $ClSO_3H$ (12.7 g) was added dropwise over about 30 minutes. An exotherm and formation of HCl was observed. The reaction was heated at 70°C under nitrogen until no more HCl could be detected (about 4 hours). A vacuum was then applied by aspirator to remove all residual HC1, and 200 g deionized water added and dioxane stripped off. The reaction mixture was neutralized to PH of 8 using 10% aqueous NH_4OH and

then diluted to 10% solids with 70/30 water/isopropanol. A clear yellow solution resulted containing the ammonium salt of the fluorochemical sulfate, $C_8F_{17}CH_2CH_2OSO_3NH_4$.

Comparative Examples 44, C12 and C13

Using the same procedure as in Example 43, Comparative Examples 44, C12 and C13 were made (as shown in Table 13).

TABLE 13

EXAMPLE	FLUOROCHEMICAL ALCOHOL USED
44(CE)	$C_8F_{17}CH_2CH_2OH$ from Example 12, containing 44% straight-chain material.
C12	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OH$ (available from 3M Company)
C13*	$C_nF_{2n+1}CH_2CH_2OH$ (n)= 8 (available from DuPont)

* A dilution to 5% had to be made using 50/50 water/isopropanol as solvent mixture in order to obtain a clear solution.

The fluorochemical ammonium sulfate salts were tested as outlined under Example 35. The results of testing are shown in Table 14.

TABLE 14

PRODUCT OF EXAMPLE	FOAM HEIGHT 500 ppm	t 1/2 (sec) 500 ppm	SURFACE TENSION (dyne/cm)	
			500 ppm	500 ppm
43	400	< 30 sec.	19.5	22.8
44(CE)	800	< 30 sec.	20.5	26.3
C12	2200	6 min. 5 sec.	17.1	18.2
C13	400	< 30 sec.	23.3	29.5

The data shows that the materials of this invention are generally low foaming and impart low surface tension.

Example 45

(See Example 1, U.S. Patent No. 4,167,639)

Into a 500 mL three-necked flask, fitted with a condenser, a thermometer, and a stirrer, were placed 52.8 g (0.2 mole) of $C_4F_9CH_2CH_2OH$ as prepared in Example 13, 9.8 g maleic anhydride (0.1 mole) and 0.2 g sulfuric acid (95%). The reaction mixture was heated under nitrogen to 140°C. Water formed in the reaction was trapped in a Dean Stark collector. After about 6 hours of reaction, 1.7 mL water was obtained. The reaction mixture was a dark brown oil containing an unsaturated diester obtained from the ring opening and esterification reaction. The reaction mixture was cooled to room temperature, and 160 g deionized water, 80 g isopropanol and 19 g (0.1 mole) sodium metabisulfite ($Na_2S_2O_5$) was added. The two-phase mixture was degassed, then heated at reflux under nitrogen for 15 hours. A clear, one-phase, brown solution was obtained containing the diester sulfosuccinate sodium salt product NMR analysis confirmed the structure to be $C_4F_9CH_2CH_2OC(O)CH_2CH(SO_3Na)C(O)OCH_2CH_2C_4F_9$. The reaction mixture was diluted to 10% solids to give a final solvent ratio of water/isopropanol = 65/35.

Example 46, Comparative Examples C14, C15

Example 46 and Comparative Examples C14 and C15 were prepared as described above in Example 44. The reactants are shown in Table 15.

TABLE 15

EXAMPLE	FLUOROCHEMICAL ALCOHOL	RATIO FC ALCOHOL TO MALEIC ANHYDRIDE*	SULFONATING AGENT
46	$C_8F_{17}CH_2CH_2OH$ (Example 12)	1:1	Na_2SO_3
C14	$C_4F_9CH_2CH_2OH$ (available from Asahi Glass, 100% linear)	2:1	$Na_2S_2O_5$
C15	$C_nF_{2n+1}CH_2CH_2OH$ (n)= 8 (available from DuPont)	1:1	Na_2SO_3

* 1:1 ratios yield monoester sulfosuccinate product; 2:1 ratios yield diestersulfosuccinate product.

The product of Examples 45, 46, and C14 and C15 were tested as described in Example 35. The results are shown in Table 16.

TABLE 16

PRODUCT OF EXAMPLE	SURFACE TENSION (dynes/cm)	
	500 ppm	100 ppm
45	17.7	24.2
46	20.1	22.0
C14	21.7	30.5
C15	20.5	29.5
Hoe S-2407*	38.8	----

* A sulfosuccinate diester sodium salt available from Hoechst.

The data shows that materials of this invention impart lower surface tension values in water than their straight-chain analogues.

Example 47

Surfactants can also be made by Michael addition of R_{fsb}-thiols of the invention to carbon-carbon double bonds containing an electron withdrawing group. Into a 500 mL three-necked flask fitted with a stirrer, thermometer, and reflux condenser, were placed 20.7 g (0.1 mole) of N-(3-sulfo-2,2-dimethylpropyl) acrylamide (AMPS), 50 g of dimethyl formamide (DMF) and 6.9 g (0.05 mole) of potassium carbonate. The mixture was stirred vigorously for 15 minutes. A clear, colorless solution resulted. Then 48.0 g (0.1 mole) of $C_8F_{17}CH_2CH_2SH$ and 0.01 g KOH were added. The reaction was heated at 70°C for 8 hours. Gas chromatography analysis indicated that virtually no starting R_{fsb}-thiol was left. A clear solution was obtained at 10% dilution using water/isopropanol 65/35 as diluent. NMR analysis confirmed the structure to be $C_8F_{17}CH_2CH_2SCH_2CH_2C(O)NHCH_2C(CH_3)_2CH_2SO_3K$.

Examples 48-51, 53-54, Comparative Examples 16, 17, 52

Examples 48-51 and 53-54 and Comparative Examples 16, 17 and 52 were prepared as in Example 47. The reactants are shown in Table 17.

TABLE 17

EXAMPLE	FLUOROCHEMICAL THIOL	UNSATURATED COMPOUND
48	$C_8F_{17}CH_2CH_2SH$ (Example 15)	AMPS - sodium salt
49	$C_8F_{17}CH_2CH_2SH$ (Example 15)	acrylic acid - sodium salt
50	$C_8F_{17}CH_2CH_2SH$ (Example 15)	Carbowax 750 acrylate (CW750 is a methoxy polyethylene glycol available from Union Carbide)
51	$C_{10}F_{21}CH_2CH_2SH$ (Example 17)	Carbowax 750 acrylate
52(CE)	$C_{10}F_{21}CH_2CH_2SH$ (Example 18)	Carbowax 750 acrylate
53	$C_8F_{17}CH_2CH_2SH$ (Example 15)	dimethylamino ethyl acrylate, quaternized with diethylsulfate
54	$C_8F_{17}CH_2CH_2SH$ (Example 15)	dimethylamino ethyl acrylate, reacted with propane sultone
C16	$C_{10}F_{21}CH_2CH_2SH$ (available from Atochem)	Carbowax 750 acrylate
C17	$C_nF_{2n+1}CH_2CH_2SH$*	Carbowax 750 acrylate

* Made from DuPont tetrahydroiodide following procedure of Example 15.

All fluorochemical surfactant materials of the above Examples and Comparative Examples were tested as described in Example 35. The results are shown in Table 18.

TABLE 18

PRODUCT OF EXAMPLE	SURFACE TENSION (dynes/cm)	
	500 ppm	100 ppm
47	19.0	24.0
48	18.7	24.0
49	17.5	21.7
50	18.5	23.4
51	17.0	19.5
52(CE)	18.7	19.8
53	18.7	19.8
54	18.1	19.5
C16	insoluble	
C17	20.0	26.8

The data shows that products of the invention impart very low surface tensions, and have good solubility, in aqueous media up to a perfluorinated chain length of 10 carbons.

Example 55

In this example, the Michael addition of amines (or polyamines) to acrylates of the invention is described. Into a 500 mL three-necked flask, fitted with a reflux condenser, a thermometer, and a stirrer, were placed 10.3 g (0.05 mole) AMPS, 80 g DMF and 3.6 g (0.025 mole) of K_2CO_3. The reaction was stirred vigorously at room temperature. A clear solution was obtained after 15 minutes. Then 25.9 g (0.05 mole of $C_8F_{17}CH_2CH_2OCOCH{=}CH_2$, as prepared in Example 20, was added followed by 3 g (0.03 mole) of ethylene diamine (EDA). An exotherm of 10°C was observed. The

reaction was heated at about 50°C for 3 hours. Gas chromatography indicated that essentially no reagents were left. The reaction mixture was diluted to 5% solids in water/isopropanol 50/50. The product mixture was tested as above in Example 35. NMR analysis confirmed the product structure to be $C_8F_{17}CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHCH_2CH_2C(O)NHCH_2C(CH_3)_2CH_2S\ O_3K$.

Examples 56-65

Examples 56-65 were prepared as in Example 55. The reactants are shown in Table 19.

TABLE 19

EX.	FLUOROCHEMICAL ACRYLATE A	AMINE B	COREAGENT C	MOLAR RATIO A/B/C
56	$C_8F_{17}CH_2CH_2OCOCH{=}CH_2$ (Example 20)	EDA[a]	$AMPS^-Na^+$	1/1/1
57	$C_8F_{17}CH_2CH_2OCOCH{=}CH_2$ (Example 20)	DMAPA[b]	$AMPS^-K^+$	1/1/1
58	$C_8F_{17}CH_2CH_2OCOCH{=}CH_2$ (Example 20)	EDA	CW750 acrylate	1/1/1
C59	$C_nF_{2n+1}CH_2CH_2OCOCH{=}CH_2$ <n> = 8 (available from DuPont)	EDA	CW750 acrylate	1/1/1
60	$C_8F_{17}CH_2CH_2OCOCH{=}CH_2$ (Example 20)	EDA	acrylic acid K^+	1/1/1
61[c]	$C_8F_{17}CH_2CH_2OCOCH{=}CH_2$ (Example 20)	EDA	DMAEMA/DES	1/1/1
62[f]	$C_8F_{17}CH_2CH_2OCOCH{=}CH_2$ (Example 20)	DMAPA	propane sultone	1/1/2
63	$C_4F_9CH_2CH_2OCOCH{=}CH_2$ (Example 21)	EDA	$AMPS^-Na^+$	2/1/1
64	$C_4F_9CH_2CH_2OCOCH{=}CH_2$ (Example 21)	DETA[d]	$AMPS^-Na^+$	3/1/1
65	$C_4F_9CH_2CH_2OCOCH{=}CH_2$ (Example 21)	TETA[c]	$AMPS^-Na^+$	4/1/3

a. EDA represents ethylene diamine

b. DMAPA represents dimethylaminopropylamine

c. DMAEMA/DES represents dimethylaminoethylacrylate, the tertiary nitrogen being quaternized with diethylsulfate (DES). Structure was confirmed by NMR to be

$[C_8F_{17}CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHCH_2CH_2C(O)OCH_2CH_2N^+(CH_3)_2 CH_2CH_3]$
$[CH_3CH_2SO_3^-]$

d. DETA represents diethylene triamine

e. TETA represents triethylene tetramine

f. NMR confirmed structure to be

$$C_8F_{17}CH_2CH_2OC(O)CH_2CH_2\underset{\displaystyle |\atop \displaystyle CH_2CH_2CH_2SO_3^-}{N^+}HCH_2CH_2CH_2N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$$

The above materials were tested as surfactants in water as in Example 35. The results are shown in Table 20.

TABLE 20

PRODUCT OF EXAMPLE	SURFACE TENSION (dynes/cm)	
	500 ppm	100 ppm
55	20.1	26.2
56	20.5	26.0
57	19.7	25.4
58	18.4	22.6
C59	18.8	25.6
60	19.0	22.7
61	19.9	21.3
62	18.9	20.7
63	18.7	25.8
64	17.5	24.5
65	22.0	29.8

The data shown that materials of the invention give very good surfactant properties.

Example 66

Into a 500 mL three-necked flask, fitted with a stirrer, a thermometer, and a reflux condenser, were placed 15 g of $C_8F_{17}CH_2CH_2OCOCH{=}CH_2$ as prepared in Example 20, 35 g of Pluronic 44 diacrylate (the diacrylate ester of Pluronic 44, a diol containing block segments of oxyethylene and oxypropylene, available from BASF), 0.3 g n-octylmercaptan, 0.3 g AIBN and 35 g ethyl acetate. The reaction was warmed to about 40°C and degassed three times using an aspirator vacuum. The reaction was heated at reflux (about 78°C) under nitrogen and continued for 15 hours. Gas chromotagraphy indicated that only traces of starting materials were left. Ethyl acetate was distilled off (aspirator vacuum) to yield a clear, viscous solution containing a fluorochemical nonionic surfactant of this invention.

Example 67

Into a 500 mL three-necked flask, fitted with a condenser, a thermometer, and a stirrer, was placed 20.7 g (0.1 mole) AMPS, 50 g DMF and 10.5 g (0.1 mole) diethanolamine under vigorous stirring at room temperature. After 15 minutes, a colorless solution was obtained. Then 9.6 g (0.02 mol) $C_8F_{17}CH_2CH_2SH$ (Example 15), was added together with 0.2 g AIBN. The reaction mixture was warmed to about 50°C and degassed using an aspirator vacuum. The reaction mixture was heated at 85°C under nitrogen for 15 hours. A clear yellow solution was obtained after filtration. NMR analysis confirmed the oligomeric product

$$C_8F_{17}CH_2CH_2S(CH_2CH)_nH$$
$$\qquad\qquad\qquad\backslash$$
$$\qquad\qquad\qquad C(O)NHCH_2C(CH_3)_2CH_2SO_3^{-\,+}NH_2(CH_2CH_2OH)_2$$

where n has an average value of about 5.

Example 68

Using the same procedure as in Example 67 but using $C_8F_{17}CH_2CH_2I$ (Example 4), in place of the thiol, another adduct of the invention was prepared,

$$C_8F_{17}CH_2CH_2(CH_2CH)_nI$$
$$\qquad\qquad\qquad /$$
$$\qquad\qquad\qquad C(O)NHCH_2C(CH_3)_2CH_2SO_3^{-\,+}NH_2(CH_2CH_2OH)_2$$

where n has an average value of about 5.

Example 69

Into a 500 mL three-necked flask of 500 mL, fitted with a reflux condenser, a thermometer, and a stirrer, were placed 23.3 g (0.05 mole) of $C_8F_{17}CH_2CH_2OH$ as prepared in Example 12, and 50 g methylethylketone (MEK). Then 20 g MEK was distilled out and trapped in a Dean Stark trap. The mixture was cooled to room temperature under nitrogen; then a Dewar condenser, filled with a dry ice/acetone mixture, was set up and 0.2 g boron trifluoride etherate complex in ether was added. Then 17.6 g (0.4 mole) of ethylene oxide were bubbled through the reaction solution over 2 hours and the reaction mixture heated at 35° to 40°C. Then the reaction was continued for 1 hour at 40°C until no reflux of ethylene oxide was observed. The reaction mixture was heated at about 70°C for 2 hours to yield a clear yellow-brown solution, containing a nonionic surfactant, $C_8F_{17}C_2H_4O(C_2H_4O)_nH$ where n has an average value of 8, as indicated by NMR and G/C analysis. All MEK was stripped off and the product was dissolved in a 70/30 mixture water/isopropanol at 10% solids. A clear yellow-brown solution resulted.

Example 70

Using the same procedure as in Example 69, a non-ionic surfactant was prepared using $C_8F_{17}CH_2CH_2SH$ (as prepared in Example 15) and a mixture of ethylene oxide and propylene oxide. The molar ratio R_{fsb} thiol/ethylene oxide/propylene oxide was 1/12/3. NMR shows the product to be primarily $C_8F_{17}CH_2CH_2S(CH_2CH_2O)_{12}(CH_2CH(CH_3)O)_3H$ where the repeating units are randomly distributed.

Example 71

In a 500 mL three-necked flask, fitted with a reflux condenser, a stirrer, and a thermometer, were placed 10.2 g (0.1 mole) of N,N dimethyl amino propylamine and 50 g ethanol. The mixture was warmed to 50°C, and 47.6 g (0.1 mole) of

$$\qquad\qquad O$$
$$\qquad\quad / \ \backslash$$
$$C_8F_{17}CH_2-CH-CH_2$$

(as prepared in Example 27), were added over 30 minutes. The heating was continued at 60°C for 2 hours. Gas chromatography indicated that all the fluorochemical epoxide was consumed. Then 0.2 mole (24.4 g) of propane sultone was added over 15 minutes. An exotherm of about 15°C was observed. The heating was continued for 2 hours at 90°C to yield a clear brown solution. The product was diluted to 10% solids using deionized water. The product was primarily

$$C_8F_{17}CH_2CH(OH)CH_2N^+H(CH_2CH_2CH_2SO_3^-)CH_2CH_2CH_2N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$$

Example 72

Into a 500 mL three-necked flask, fitted with a stirrer, a reflux condenser, and a thermometer, were placed 4.9 g (0.05 mole) maleic anhydride, 10 g methyl ethyl ketone and 37.5 g (0.05 mole) of dry Carbowax 750 (a methoxypolyethylene glycol available from Union Carbide). The mixture was heated at 70°C for 16 hours. After this period, no anhydride peak in the infrared spectrum could be detected. Then 24 g (0.05 mole) of $C_8F_{17}CH_2CH_2SH$, as prepared in Example 15, were added together with 0.4 g triethylamine catalyst. Heating was continued for 16 hours at 60°C to yield a clear yellow-brown reaction solution. Gas chromatography indicated that only traces of thiol were left. Then the MEK was stripped off and the reaction product was dissolved in a 70/30 mixture of water/isopropanol at 10% solids. A clear solution containing a mixed anionic-nonionic surfactant was prepared by adding 4 g (0.05 mole) of a 50% NaOH solution in water. The product was a mixture of $C_8F_{17}CH_2CH_2SCH(CO_2Na)CH_2C(O)O(CH_2CH_2O)_nCH_3$ and $C_8F_{17}CH_2CH_2SCH(CH_2CO_2Na)C(O)O(CH_2CH_2O)_nCH_3$, where n has an average value of about 16.

The products of Examples 66 to 72 were tested as surfactants in water (at 500 ppm) as in Example 35. The results are shown in Table 21.

TABLE 21

PRODUCT OF EXAMPLE	NATURE OF SURFACTANT	SURFACE TENSION (dynes/cm)
66	oligomeric nonionic	32.1
67	oligomeric anionic	25.7
68	oligomeric anionic	23.5
69	nonionic	21.7
70	nonionic	23.1
71	amphoteric	17.5
72	mixture of anionic + nonionic	20.7

The data shows that surfactants of this invention exhibit very good aqueous surface tension properties, regardless of the nature of the polar group, i.e. ionic or nonionic, or of molecular weight.

Various modifications and variations of this invention will become apparent to those skilled in the art without departing from the scope of this invention.

Claims

1. Fluorochemical composition comprising a mixture of compounds wherein said mixture comprises compounds of the general formula R_{fs}-$CH_2CH(R^1)$-R^2-X and compounds of the general formula R_{fb}-$CH_2CH(R^1)$-R^2-X; wherein R_{fs}- is a straight-chain perfluoroalkyl group and R_{fb}- is a branched-chain perfluoroalkyl group; -$CH_2CH(R^1)$-R^2- is a fluorine-free alkylene linking group where R^1 is selected from H a lower organic moiety of 1 to 4 carbon atoms, a phenyl group, and combinations of said lower organic moiety and said phenyl group provided that R^1 may also contain heteroatoms, and wherein R^2 is selected from a covalent bond, an alkylene group of 0 to 20 carbon atoms, and -CH(R)- where R is as defined for R^1 provided that R^2 may also contain heteroatoms; and x is a halogen atom selected from Cl, Br and I; and wherein in from 50 to 95% of said compounds the perfluoroalkyl group is straight-chain and in all others of said compound said perfluoroalkyl group is branched-chain.

2. The fluorochemical composition of claim 1 wherein the perfluoroalkyl groups consist predominately of the same number of carbon atoms per perfluoroalkyl group, and wherein the perfluoroalkyl group contains from 4 to 20 fully

fluorinated carbon atoms.

3. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds, or polymers of, or adducts of compounds of the general formula R_{fs}-CH_2CH_2-OC(O)CR=CH_2 and compounds of the general formula R_{fb}-CH_2CH_2-OC(O)CR=CH_2 where R is H or CH_3; and wherein -CH_2CH_2- comprises said retained two carbon atoms.

4. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds of the general formula $C_3N_6(CH_2OCH_3)_x[CH_2SCH_2CH_2\text{-}R_{fs}]_y$ and compounds of the general formula $C_3N_6(CH_2OCH_3)_x[CH_2SCH_2CH_2\text{-}R_{fb}]_y$ where x + y is 6; and wherein -CH_2CH_2- comprises said retained two carbon atoms.

5. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds, or derivatives of compounds, of the general formula R_{fs}-CH_2CH_2-OH and compounds of the general formula R_{fb}-CH_2CH_2-OH; and wherein -CH_2CH_2- comprises said retained two carbon atoms; and wherein -OH is a functional group.

6. The fluorochemical composition of claim 5, wherein said derivatives of compounds comprise the reaction products of said compounds and an organic isocyanate.

7. The fluorochemical composition of claim 6, wherein said isocyanate comprises $OCNC_6H_4CH_2[C_6H_3(NCO)]_nCH_2C_6H_4NCO$, where the average of n is between 0.5 and 1.0.

8. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds, or derivatives of compounds, of the general formula R_{fs}-CH_2CH_2-SH and compounds of the general formula R_{fb}-CH_2CH_2-SH; and wherein -CH_2CH_2- comprises said retained two carbon atoms.

9. The fluorochemical composition of claim 8, wherein said derivatives of compounds comprise the reaction product of said compounds and an unsaturated alcohol selected from the group consisting of propargyl alcohol and 2,4-hexadiyne-1,6-diol.

10. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds of the general formula $[R_{fs}\text{-}CH_2CH_2\text{-}O]_nP(O)(OH)_{3-n}$ and compounds of the general formula $[R_{fb}\text{-}CH_2CH_2\text{-}O]_nP(O)(OH)_{3-n}$ where n is from 1 to 2, or the sodium, potassium, or ammonium salts thereof; and wherein -CH_2CH_2- comprises said retained two carbon atoms.

11. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms

from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds of the general formula R_{fs}-CH_2CH_2-$OC(O)CH(OH)CH_2COO$-CH_2CH_2-R_{fs} and compounds of the general formula R_{fs}-CH_2CH_2-$OC(O)CH(OH)CH_2COO$-CH_2CH_2-R_{fb} and compounds of the general formula R_{fb}-CH_2CH_2-$OC(O)CH(OH)CH_2COO$-CH_2CH_2-R_{fb} and compounds of the general formula R_{fb}-CH_2CH_2-$OC(O)CH(OH)CH_2COO$-CH_2CH_2-R_{fs}, or the phosphate ester derivatives thereof; and wherein -CH_2CH_2- comprises said retained two carbon atoms.

12. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds of the general formula R_{fs}-$CH_2CH_2OC(O)CH{=}CHCOO$-CH_2CH_2-R_{fs} and compounds of the general formula R_{fs}-CH_2CH_2-$OC(O)CH{=}CHCOO$-CH_2CH_2-R_{fb} and compounds of the general formula R_{fb}-$CH_2CH_2OC(O)CH{=}CHCOO$-CH_2CH_2-R_{fb} and compounds of the general formula R_{fb}-CH_2CH_2-$OC(O)CH{=}CHCOO$-CH_2CH_2-R_{fs}, or the sulfosuccinate sodium salts thereof; and wherein -CH_2CH_2- comprises said retained two carbon atoms.

13. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds, or derivatives, of compounds, of the general formula R_{fs}-CH_2CH_2-OSO_3NH_4 and compounds of the general formula R_{fb}-CH_2CH_2-OSO_3NH_4; and wherein -CH_2CH_2- comprises said retained two carbon atoms.

14. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds, or derivatives, of compounds, of the general formula R_{fs}-CH_2CH_2-S-$CH_2CH_2C(O)NHCH_2C(CH_3)_2CH_2SO_3H$ and compounds of the general formula R_{fb}-CH_2CH_2-S-$CH_2CH_2C(O)NHCH_2C(CH_3)_2CH_2SO_3H$, and salts thereof.

15. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds of the general formula R_{fs}-CH_2CH_2-S-CH_2-COOH, and compounds of the general formula R_{fb}-CH_2CH_2-S-CH_2-COOH or salts thereof; and wherein -CH_2CH_2- comprises said retained two carbon atoms.

16. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds of the general formula R_{fs}-CH_2CH_2-S-CH_2CH_2-$C(O)OC_2H_4O(C_2H_4O)_nCH_3$ and compounds of the general formula R_{fb}-CH_2CH_2-S-$CH_2CH_2C(O)OC_2H_4O(C_2H_4O)_nCH_3$ where n has a value of 1 to about 30.

17. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms

from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds of the general formula R_{fs}-CH_2CH_2-SCH_2CH_2-$C(O)OC_2H_4N^+(CH_3)_2C_2H_5C_2H_5OSO_3$- and compounds of the general formula R_{fb}-CH_2CH_2-S-CH_2CH_2-$C(O)OC_2H_4N^+(CH_3)_2C_2H_5C_2H_5OSO_3$-.

18. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds, or derivatives, of compounds, of the general formula R_{fs}-CH_2CH_2-S-$CH_2CH_2C(O)OC_2H_4N^+(CH_3)_2CH_2CH_2CH_2SO_3$- and compounds of the general formula R_{fb}-CH_2CH_2-S-CH_2CH_2-$C(O)OC_2H_4N^+(CH_3)_2CH_2CH_2CH_2SO_3$-.

19. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds, or derivatives, of compounds, of the general formula R_{fs}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHC_2H_4C(O)NHCH_2C(CH_3)_2CH_2$-$SO_3H$ and compounds of the general formula R_{fb}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHC_2H_4C(O)NHCH_2C(CH_3)_2CH_2$-$SO_3H$, or salts thereof.

20. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds, or derivatives, of compounds, of the general formula R_{fs}-$CH_2CH_2OC(O)CH_2CH_2N[CH_2CH_2CH_2N(CH_3)_2]C_2H_4C(O)NHCH_2C$-$(CH_3)_2CH_2SO_3H$ and compounds of the general formula R_{fb}-$CH_2CH_2OC(O)CH_2CH_2N[CH_2CH_2CH_2N(CH_3)_2]C_2H_4C(O)NHCH_2C$-$(CH_3)_2CH_2SO_3H$, or salts thereof.

21. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds, or derivatives, of compounds, of the general formula R_{fs}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHC_2H_4C(O)OC_2H_4O(C_2H_4O)_nCH_3$ and compounds of the general formula R_{fb}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHC_2H_4C(O)OC_2H_4O(C_2H_4O)_nCH_3$ where n is 1 to about 30 or higher.

22. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds, or derivatives, of compounds, of the general formula R_{fs}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHC_2H_4COOH$ and compounds of the general formula R_{fb}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHC_2H_4COOH$ or salts thereof.

23. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds, or derivatives of compounds, of the general formula R_{fs}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHCH_2C_2C(O)$-$OC_2H_4N^+(CH_3)_2C_2H_5C_2H_5OSO_3^-$ and compounds of the general formula R_{fb}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHCH_2CH_2C(O)$-$OC_2H_4N^+(CH_3)_2C_2H_5C_2H_5OSO_3^-$.

24. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds, or derivatives, of compounds, of the general formula R_{fs}-$CH_2CH_2OC(O)CH_2CH_2N^+(H)[C_3H_6SO_3^-]C_2H_4N^+(CH_3)$ and compounds of the general formula R_{fb}-$CH_2CH_2OC(O)CH_2CH_2N^+(H)[C_3H_6SO_3^-]C_2H_4N^+(CH_3)$.

25. Fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said mixture of derivatives comprises compounds, or derivatives, of compounds, of the general formula R_{fs}-$CH{=}CH_2$ and compounds of the general formula R_{fb}-$CH{=}CH_2$, and polymers thereof.

26. A polymer composition comprising a mixture of polymers comprising interpolymerized units derived from a mixture of compounds wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain,

wherein said polymers comprise a polymeric chain with a plurality of pendant saturated perfluoroalkyl groups wherein 50 to 95% of said perfluoroalkyl groups are straight and all others of said perfluoroalkyl groups are branched; and wherein said perfluoroalkyl groups are bonded directly to the polymer chain or are bonded to an alkylene carbon atom.

27. The polymer composition of claim 26 wherein said mixture of polymers comprises polyacrylate homopolymers or copolymers.

28. A method for modifying the surface properties of a substrate, which comprises contacting the surface of said substrate with the polymer composition of any one of preceding claims 26-27.

29. A method for modifying the surface tension or interfacial tension of a body of liquid, which comprises adding thereto an amount of a fluorochemical composition sufficient to obtain the desired modified surface tension or interfacial tension of said liquid, wherein said fluorochemical composition comprises a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain.

30. A method for modifying the surface properties of a substrate, which comprises contacting the surface of said substrate with a composition comprising a fluorochemical composition wherein said fluorochemical composition comprises a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain.

31. A substrate having a surface thereof modified by a fluorochemical composition wherein said fluorochemical composition comprises a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain.

32. The substrate of claim 31, wherein said substrate comprises textile, paper, or leather.

33. A body of liquid comprising a fluorochemical composition, said fluorochemical composition comprising a mixture of compounds, wherein said compounds are derivatives of a precursor-mixture comprising the compositions of claim 1; and wherein said derivatives retain at least 2 carbon atoms from the alkylene linking group, and where said derivatives retain the perfluoroalkyl group wherein in 50 to 95% of said derivatives the perfluoroalkyl group is straight-chain and in all others of said derivatives the perfluoroalkyl group is branched-chain.

34. A process for the preparation of the fluorochemical composition of claim 1 comprising reacting ethylene with a precursor mixture of perfluoroalkyl iodides, or perfluoroalkyl sulfonylchlorides, or perfluoroalkyl sulfonylbromides; wherein in from 50 to 95% of said precursors said perfluoroalkyl is straight-chain and in all others of said precursors said perfluoroalkyl is branched-chain.

35. The process of claim 34, wherein said precursor mixture is prepared by electrochemical fluorination of the hydrocarbon analog.

Patentansprüche

1. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Mischung umfaßt: Verbindungen der allgemeinen Formel R_{fs}-$CH_2CH(R^1)$-R^2-X und Verbindungen der allgemeinen Formel R_{fb}-$CH_2CH(R^1)$-R^2-X, worin R_{fs}- eine geradkettige Perfluoralkyl-Gruppe und R_{fb}- eine verzweigtkettige Perfluoralkyl-Gruppe sind; -$CH_2CH(R^1)$-R^2- eine fluorfreie, Alkylen-verknüpfende Gruppe, worin R^1 ausgewählt wird aus Wasserstoff oder einem niederen organischen Teil mit 1 ... 4 Kohlenstoff-Atomen, einer Phenyl-Gruppe und Kombinationen des niederen organischen Teils und der Phenyl-Gruppe unter der Voraussetzung, daß R^1 auch Heteroatome enthalten kann, und worin R^2 ausgewählt wird aus einer kovalenten Bindung, einer Alkylen-Gruppe mit Null bis 20 Kohlenstoff-Atomen und -CH(R)-, worin R wie für R^1 festgelegt ist unter der Voraussetzung, daß R^2 ebenfalls Heteroatome enthält; und wobei x ein Halogen-Atom ist, Ausgewählt aus Cl, Br J; und wobei in 50 ... 95 % der Verbindungen die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist.

2. Fluorchemische Zusammensetzung nach Anspruch 1, wobei die Perfluoralkyl-Gruppen überwiegend aus der gleichen Zahl von Kohlenstoff-Atomen pro Perfluoralkyl-Gruppe bestehen und wobei die Perfluoralkyl-Gruppe 4 ... 20 vollständig fluorierte Kohlenstoff-Atome enthält.

3. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und wobei die Mischung der Derivate Verbindungen oder Polymere oder Addukte von Verbindungen der allgemeinen Formel

R_{fs}-CH_2CH_2-OC(O)CR=CH_2

sowie Verbindungen der allgemeinen Formel

R_{fb}-CH_2CH_2-OC(O)CR=CH_2

umfaßt, worin R Wasserstoff oder CH_3 ist und worin -CH_2CH_2-die zwei behaltenen Kohlenstoff-Atome umfaßt.

4. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen der allgemeinen Formel umfaßt:

$C_3N_6(Ch_2OCH_3)_x[CH_2SCH_2CH_2\text{-}R_{fs}]_y$

sowie Verbindungen der allgemeinen Formel

$C_3N_6(Ch_2OCH_3)_x[CH_2SCH_2CH_2\text{-}R_{fb}]_y$

worin x+y 6 beträgt und worin -CH_2CH_2- die zwei behaltenen Kohlenstoff-Atome umfaßt.

5. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die

Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen oder Derivate von Verbindungen der allgemeinen Formel R_{fs}-CH_2CH_2-OH und Verbindungen der allgemeinen Formel R_{fb}-CH_2CH_2-OH umfaßt, und worin -CH_2CH_2- die zwei behaltenen Kohlenstoff-Atome umfaßt.

6. Fluorchemische Zusammensetzung nach Anspruch 5, bei welcher die Derivate von Verbindungen die Reaktionsprodukte von der Verbindungen und ein organisches Isocyanat umfassen.

7. Fluorchemische Zusammensetzung nach Anspruch 6, mit dem Isocyanat:
$OCNC_6H_4CH_2[C_6H_3(NCO)]_nCH_2C_6H_4NCO$
worin der Mittelwert für n zwischen 0,5 ... 1,0 liegt.

8. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen oder Derivate von Verbindungen der allgemeinen Formel R_{fs}-CH_2CH_2-SH und Verbindungen der allgemeinen Formel R_{fb}-CH_2CH_2-SH umfaßt, und worin -CH_2CH_2- die zwei behaltenen Kohlenstoff-Atome umfaßt.

9. Fluorchemische Zusammensetzung nach Anspruch 8, bei welcher die Derivate der Verbindungen das Reaktionsprodukt der Verbindungen und einen ungesättigten Alkohol umfassen, ausgewählt aus der Gruppe, bestehend aus Propargylalkohol und 2,4-Hexadiin-1,6-diol.

10. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen allgemeinen Formel $[R_{fs}\text{-}CH_2CH_2\text{-}O]_nP(O)(OH)_{3-n}$ und Verbindungen der allgemeinen Formel$[R_{fb}\text{-}CH_2CH_2\text{-}O]_nP(O)(OH))_{3-n}$ umfaßt, worin n 1 ... 2 beträgt, oder Natrium-, Kalium- oder Ammonium-Salze davon; und worin -CH_2CH_2- die zwei behaltenen Kohlenstoff-Atome umfaßt.

11. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen der allgemeinen Formeln umfaßt:
R_{fs}-CH_2CH_2-O-C(O)CH(OH)CH_2COO-CH_2CH_2-R_{fs};
R_{fs}-CH_2CH_2-O-C(O)CH(OH)CH_2COO-CH_2CH_2-R_{fb};
R_{fb}-CH_2CH_2-O-C(O)CH(OH)CH_2COO-CH_2CH_2-R_{fb};
R_{fb}-CH_2CH_2-O-C(O)CH(OH)CH_2COO-CH_2CH_2-R_{fs};
oder die Phosphatester-Derivate davon; und worin -CH_2CH_2- die zwei behaltenen Kohlenstoff-Atome umfaßt.

12. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen der allgemeinen Formeln umfaßt:
R_{fs}-CH_2CH_2OC(O)CH=CHCOO-CH_2CH_2-R_{fs};
R_{fs}-CH_2CH_2OC(O)CH=CHCOO-CH_2CH_2-R_{fb};
R_{fb}-CH_2CH_2OC(O)CH=CHCOO-CH_2CH_2-R_{fb};
R_{fb}-CH_2CH_2OC(O)CH=CHCOO-CH_2CH_2-R_{fs};
oder die Sulfosuccinat-Salze davon; und worin -CH_2CH_2- die zwei behaltenen Kohlenstoff-Atome umfaßt.

13. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen oder Derivate von Verbindungen der allgemeinen Formeln R_{fs}-CH_2CH_2-OSO_3NH_4 und R_{fs}-CH_2CH_2-OSO_3NH_4 umfaßt und worin -CH_2CH_2- die zwei behaltenen Kohlenstoff-Atome umfaßt.

14. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen oder Derivate von Verbindungen der allgemeinen Formeln
R_{fs}-CH_2CH_2-S-$CH_2CH_2C(O)NHCH_2C(CH_3)_2CH_2SO_3H$ und
R_{fb}-CH_2CH_2-S-$CH_2CH_2C(O)NHCH_2C(CH_3)_2CH_2SO_3H$ umfaßt.

15. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen oder Derivate von Verbindungen der allgemeinen Formeln R_{fs}-CH_2CH_2-S-CH_2-COOH und R_{fb}-CH_2CH_2-S-CH_2-COOH oder Salze davon umfaßt und worin -CH_2CH_2- die zwei behaltenen Kohlenstoff-Atome umfaßt.

16. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen oder Derivate von Verbindungen der allgemeinen Formeln
R_{fs}-CH_2CH_2-S-CH_2CH_2-$C(O)OC_2H_4O(C_2H_4O)_nCH_3$ und
R_{fb}-CH_2CH_2-S-CH_2CH_2-$C(O)OC_2H_4O(C_2H_4O)_nCH_3$ umfaßt und worin n einen Wert von 1 bis etwa 30 hat.

17. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen der allgemeinen Formeln umfaßt
R_{fs}-CH_2CH_2-SCH_2CH_2-$C(O)OC_2H_4N^+(CH_3)_2C_2H_5C_2H_5OSO_3^-$ und
R_{fb}-CH_2CH_2-SCH_2CH_2-$C(O)OC_2H_4N^+(CH_3)_2C_2H_5C_2H_5OSO_3^-$.

18. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen oder Derivate von Verbindungen der allgemeinen Formeln umfaßt:
R_{fs}-CH_2CH_2-S-CH_2CH_2-$C(O)OC_2H_4N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$ und
R_{fb}-CH_2CH_2-S-CH_2CH_2-$C(O)OC_2H_4N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$.

19. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in

allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen oder Derivate von Verbindungen der allgemeinen Formeln umfaßt:

R_{fs}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHC_2H_4C(O)NHCH_2C(CH_3)_2CH_2SO_3H$ und
R_{fb}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHC_2H_4C(O)NHCH_2C(CH_3)_2CH_2SO_3H$ oder Salze davon.

20. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen oder Derivate von Verbindungen der allgemeinen Formeln umfaßt:

R_{fs}-$CH_2CH_2OC(O)CH_2CH_2N[CH_2CH_2CH_2N(CH_3)_2]C_2H_4C(O)NHCH_2C(CH_3)_2CH_2SO_3H$ und
R_{fb}-$CH_2CH_2OC(O)CH_2CH_2N[CH_2CH_2CH_2N(CH_3)_2]C_2H_4C(O)NHCH_2C(CH_3)_2CH_2SO_3H$ oder Salze davon.

21. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen oder Derivate von Verbindungen der allgemeinen Formeln umfaßt:

R_{fs}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHC_2H_4C(O)OC_2H_4O(C_2H_4O)_nCH_3$ und
R_{fb}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHC_2H_4C(O)OC_2H_4O(C_2H_4O)_nCH_3$
worin n 1 bis etwa 30 ist.

22. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen oder Derivate von Verbindungen der allgemeinen Formeln umfaßt:

R_{fs}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHC_2H_4COOH$ und
R_{fs}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHC_2H_4COOH$ oder Salze davon.

23. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen oder Derivate von Verbindungen der allgemeinen Formeln umfaßt:

R_{fs}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHCH_2C_2C(O)OC_2H_4N^+(CH_3)_2C_2H_5C_2H_5OSO_3^-$ und
R_{fb}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHCH_2C_2C(O)OC_2H_4N^+(CH_3)_2C_2H_5C_2H_5OSO_3^-$

24. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen oder Derivate von Verbindungen der allgemeinen Formeln umfaßt:

R_{fs}-$CH_2CH_2OC(O)CH_2CH_2N^+(H)[C_3H_6SO_3^-]C_2H_4N^+(CH_3)$ und
R_{fb}-$CH_2CH_2OC(O)CH_2CH_2N^+(H)[C_3H_6SO_3^-]C_2H_4N^+(CH_3)$.

25. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate

mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und

wobei die Mischung der Derivate Verbindungen oder Derivate von Verbindungen der allgemeinen Formeln R_{fs}-CH=CH_2 und R_{fb}-CH=CH_2 umfaßt sowie Polymere davon.

26. Fluorchemische Zusammensetzung, umfassend ein Mischung von Verbindungen, wobei die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist und worin die Polymere eine Polymerkette mit einer Vielzahl gesättigten Perfluoralkyl-Seitengruppen umfassen, worin 50 ... 95 % der Perfluoralkyl-Gruppen geradkettig sind und alle anderen Perfluoralkyl-Gruppen verzweigtkettig sind und worin die Perfluoralkyl-Gruppen direkt an der Polymerkette gebunden sind oder an einem Alkylen-Kohlenstoffatom gebunden sind.

27. Polymer-Zusammensetzung nach Anspruch 26, bei der die Mischung der Polymere Polyacrylat-Homopolymere oder - Copolymere umfaßt.

28. Verfahren zum Modifizieren der Oberflächeneigenschaften eines Substrats, umfassend das Kontaktieren der Oberfläche des Substrats mit der Polymer-Zusammensetzung nach einer der vorgenannten Ansprüche 26 und 27.

29. Verfahren zum Modifizieren der Oberflächenspannung oder Grenzflächenspannung eines Körpers einer Flüssigkeit, umfassend das Zusetzen dazu einer ausreichenden Menge einer fluorchemischen Zusammensetzung, um die angestrebte Oberflächenspannung oder Grenzflächenspannung der Flüssigkeit zu erhalten, wobei die fluorchemischen Zusammensetzung eine Mischung von Verbindungen umfaßt, bei welcher die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist.

30. Verfahren zum Modifizieren der Oberflächeneigenschaften eines Substrats, umfassend das Kontaktieren der Oberfläche des Substrats mit einer Zusammensetzung, umfassend eine fluorchemischen Zusammensetzung wobei die fluorchemischen Zusammensetzung eine Mischung von Verbindungen umfaßt, bei welcher die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist.

31. Substrat mit einer Oberfläche, modifiziert durch eine fluorchemische Zusammensetzung, wobei die fluorchemischen Zusammensetzung eine Mischung von Verbindungen umfaßt, bei welcher die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist.

32. Substrat nach Anspruch 31, welches Substrat Textilien, Papier oder Leder umfaßt.

33. Körper einer Flüssigkeit, umfassend eine fluorchemische Zusammensetzung, wobei die fluorchemischen Zusammensetzung eine Mischung von Verbindungen umfaßt, bei welcher die Verbindungen Derivate einer Präkursor-Mischung sind, umfassend die Zusammensetzung nach Anspruch 1; und wobei die Derivate mindestens zwei Kohlenstoff-Atome aus der Alkylen-verknüpfenden Gruppe behalten und wobei die Derivate die Perfluoralkyl-Gruppe behalten, wobei in 50 ... 95 % der Derivate die Perfluoralkyl-Gruppe geradkettig ist und in allen anderen der genannten Verbindung die Perfluoralkyl-Gruppe verzweigtkettig ist.

34. Verfahren zu Darstellung fluorchemischen Zusammensetzung nach Anspruch 1, umfassend das Umsetzen von Ethylen mit einer Präkursor-Mischung von Perfluoralkyl-Iodiden oder Perfluoralkyl-Sulfonylchloriden oder Perfluoralkyl-Sulfonylbromiden, wobei in 50 ... 95 % der Präkursoren das Perfluoralkyl geradkettig und in allen anderen der Präkursoren das Perfluoralkyl verzweigtkettig ist.

35. Verfahren nach Anspruch 34, bei welchem die Präkursor-Mischung durch elektrochemische Fluorierung des Kolenwasserstoff-Analogon dargestellt wird.

Revendications

1. Composition fluorochimique comprenant un mélange de composés dans laquelle ledit mélange comprend des composés de la formule générale R_{fs}-$CH_2CH(R^1)$-R^2-X et des composés de la formule générale F_{fb}-$CH_2CH(R^1)$-R^2)-X, dans lesquelles R_{fs}- est un groupe perfluoroalkyle à chaîne droite et F_{fb}- est un groupe perfluoroalkyle à chaîne ramifiée, -$CH_2CH(R^1)$-R^2- est un groupe de liaison d'alkylène sans fluor dans lequel R^1 est choisi parmi H, un fragment organique inférieur de 1 à 4 atomes de carbone, un groupe phényle et des combinaisons de ce fragment organique inférieur et de ce groupe phényle pour autant que R^1 puisse également contenir des hétéroatomes, et dans lequel R^2 est choisi parmi une liaison covalente, un groupe alkylène de 0 à 20 atomes de carbone et -CH-(R)- où R est tel que défini pour R^1 pour autant que R^2 puisse également contenir des hétéroatomes, et X est un atome d'halogène choisi parmi Cl, Br et I, et dans laquelle dans de 50 à 95 % de ces composés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres composés ce groupe perfluoroalkyle est à chaîne ramifiée.

2. Composition fluorochimique suivant la revendication 1, dans laquelle les groupes perfluoroalkyle se composent essentiellement du même nombre d'atomes de carbone par groupe perfluoroalkyle et dans laquelle le groupe perfluoroalkyle contient de 4 à 20 atomes de carbone totalement fluorés.

3. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1 et dans laquelle lesdits dérivés conservent au moins deux atomes de carbone du groupe de liaison d'alkylène et où ces dérivés conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, et dans laquelle le mélange susdit de dérivés comprend des composés ou des polymères ou des produits d'addition de composés de la formule générale R_{fs}-CH_2CH_2-OC(O)CR=CH_2 et de composés de la formule générale R_{fb}-CH_2CH_2-OC(O)CR=CH_2 où R est H ou CH_3 et dans lesquelles -CH_2CH_2- comprend les deux atomes de carbone conservés précités.

4. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1 et dans laquelle ces dérivés conservent au moins 2 atomes de carbones du groupe de liaison d'alkylène et où lesdits dérivés conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange susdit de dérivés comprend des composés de la formule générale $C_3N_6(CH_2OCH_3)_x[CH_2SCH_2CH_2\text{-}R_{fs}]_y$ et des composés de la formule générale $C_3N_6(CH_2OCH_3)_x[CH_2SCH_2CH_2\text{-}R_{fb}]_y$ où x + y est égal à 6, et dans lesquelles -CH_2CH_2-comprend les 2 atomes de carbone conservés.

5. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1, et dans laquelle ces dérivés conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène, et où ces dérivés conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés ou des dérivés de composés de la formule générale R_{fs}-CH_2CH_2-OH et de composés de la formule générale R_{fb}-CH_2CH_2-OH et dans lesquelles -CH_2CH_2- comprend les 2 atomes de carbone conservés précités et où OH est un groupe fonctionnel.

6. Composition fluorochimique suivant la revendication 5, dans laquelle les dérivés de composés précités comprennent les produits réactionnels de ces composés et d'un isocyanate organique.

7. Composition fluorochimique suivant la revendication 6, dans laquelle l'isocyanate comprend $OCNC_6H_4CH_2[C_6H_3(NCO)]_nCH_2C_6H_4NCO$, où la moyenne de n se situe entre 0,5 et 1,0.

8. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendications 1, et dans laquelle ces dérivés conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène et où les dérivés précités conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés ou des dérivés de composés de la formule générale R_{fs}-CH_2CH_2-SH et de com-

posés de la formule générale R_{fb}-CH_2CH_2-SH et dans lesquelles -CH_2CH_2- comprend les 2 atomes de carbone conservés précités.

9. Composition fluorochimique suivant la revendication 8, dans laquelle les dérivés de composés précités comprennent le produit réactionnel de ces composés et d'un alcool insaturé choisi dans le groupe comprenant l'alcool propargylique et le 2,4-hexadiyne-1,6-diol.

10. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1 et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène et où ces dérivés conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés de la formule générale $[R_{fs}$-$CH_2CH_2O]_nP(O)(OH)_{3-n}$ et des composés de la formule générale $[R_{fb}$-$CH_2CH_2O]_nP(O)(OH)_{3-n}$ où n vaut de 1 à 2 ou leurs sels de sodium, de potassium ou d'ammonium, et où -CH_2CH_2- comprend les 2 atomes de carbone conservés précités.

11. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1 et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène et où ces dérivés conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés de la formule générale R_{fs}-CH_2CH_2-OC(O)CH(OH)CH_2COO-CH_2CH_2-R_{fs} et des composés de la formule générale R_{fs}-CH_2CH_2-OC(O)CH-(OH)CH_2COO-CH_2CH_2-R_{fb} et des composés de la formule générale R_{fb}-CH_2CH_2-OC(O)CH(OH)CH_2COO-CH_2CH_2-R_{fb} et des composés de la formule générale R_{fb}-CH_2CH_2-OC(O)CH(OH)CH_2-COO-CH_2CH_2-R_{fs} ou leurs dérivés esters de phosphate et où -CH_2CH_2- comprend les deux atomes de carbone conservés précités.

12. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1, et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène, et où ces dérivés conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés de la formule générale R_{fs}-CH_2CH_2-OC(O)CH=CHCOO-CH_2CH_2-R_{fs} et des composés de la formule générale R_{fs}-CH_2CH_2-OC(O)CH=CHCOO-CH_2CH_2-R_{fb} et des composés de la formule générale R_{fb}-CH_2CH_2-OC(O)CH=CHCOO-CH_2CH_2-R_{fb} et des composés de la formule générale R_{fb}-CH_2CH_2-OC(O)CH=CHCOO-CH_2CH_2-R_{fs} ou leurs sels sodiques de sulfosuccinate et où -CH_2CH_2-comprend les deux atomes de carbone conservés précités.

13. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1, et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène, et où ces dérivés conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés ou des dérivés de composés de la formule générale R_{fs}-CH_2CH_2-OSO_3NH_4 et des composés de la formule générale F_{fb}-CH_2CH_2-OSO_3NH_4 et où -CH_2CH_2- comprend les deux atomes de carbone conservés précités.

14. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1, et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène, et où les dérivés précités conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés ou des dérivés de composés de la formule générale R_{fs}-CH_2CH_2-S-CH_2CH_2C(O)NHCH_2C$(CH_3)_2CH_2SO_3H$ et de composés de la formule générale R_{fb}-CH_2CH_2-S-CH_2CH_2C(O)NH-CH_2C$(CH_3)_2CH_2SO_3H$ et leurs sels.

15. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1, et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène, et où les dérivés précités

conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés de la formule générale F_{fs}-CH_2CH_2-S-CH_2-COOH et des composés de la formule générale F_{fb}-CH_2CH_2-S-CH_2-COOH ou leurs sels, et où -CH_2CH_2- comprend les deux atomes de carbone conservés précités.

16. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1, et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène, et où les dérivés précités conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés de la formule générale R_{fs}-CH_2CH_2-S-$CH_2CH_2C(O)$-$OC_2H_4O(C_2H_4O)_nCH_3$ et des composés de la formule générale R_{fb}-CH_2CH_2-S-$CH_2CH_2C(O)OC_2H_4O(C_2H_4O)_nCH_3$, où n a une valeur de 1 à environ 30.

17. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1, et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène, et où les dérivés précités conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés de la formule générale R_{fs}-CH_2CH_2-SCH_2CH_2-C(O)-$OC_2H_4N^+(CH_3)_2C_2H_5C_2H_5OSO_3^-$ et des composés de la formule générale R_{fb}-CH_2CH_2-S-CH_2CH_2-$C(O)OC_2H_4N^+(CH_3)_2C_2H_5C_2H_5OSO_3^-$.

18. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1, et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène, et où les dérivés précités conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés ou des dérivés de composés de la formule générale R_{fs}-CH_2CH_2-S-$CH_2CH_2C(O)OC_2H_4N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$ et de composés de la formule générale R_{fb}-CH_2CH_2-S-CH_2CH_2-C(O)-$OC_2H_4N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$.

19. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1, et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène, et où les dérivés précités conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés ou des dérivés de composés de la formule générale R_{fs}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHC_2H_4C(O)NHCH_2$-$C(CH_3)_2CH_2$-$SO_3H$ et de composés de la formule générale $R_{fb}CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHC_2H_4C(O)NHCH_2C(CH_3)_2CH_2$-$SO_3H$ ou leurs sels.

20. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1, et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène, et où les dérivés précités conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés ou des dérivés de composés de la formule générale R_{fs}-$CH_2CH_2OC(O)CH_2CH_2N[CH_2CH_2CH_2N(CH_3)_2]C_2H_4$-$C(O)NHCH_2C(CH_3)_2CH_2SO_3H$ et de composés de la formule générale R_{fb}-$CH_2CH_2OC(O)CH_2CH_2N[CH_2CH_2CH_2N(CH_3)_2]C_2H_4$-$C(O)NHCH_2C(CH_3)_2CH_2SO_3H$ ou leurs sels.

21. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1, et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène, et où les dérivés précités conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés ou des dérivés de composés de la formule générale R_{fs}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHC_2H_4C(O)OC_2H_4O(C_2H_4O)_nCH_3$ et de composés de la formule générale

R_{fb}-$CH_2CH_2OC(O)CH_2$-$CH_2NHCH_2CH_2NHC_2H_4C(O)OC_2H_4O(C_2H_4O)_nCH_3$, où n vaut de 1 à environ 30 ou plus.

22. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1, et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène, et où les dérivés précités conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés ou des dérivés de composés de la formule générale R_{fs}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHC_2H_4COOH$ et de composés de la formule générale R_{fb}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2$-$CH_2NHC_2H_4COOH$ ou leurs sels.

23. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1, et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène, et où les dérivés précités conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés ou des dérivés de composés de la formule générale R_{fs}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHCH_2CH_2C(O)OC_2H_4N^+$-$(CH_3)_2C_2H_5C_2H_5OSO_3^-$ et de composés de la formule générale R_{fb}-$CH_2CH_2OC(O)CH_2CH_2NHCH_2CH_2NHCH_2CH_2C(O)OC_2H_4N^+(CH_3)_2C_2H_5$-$C_2H_5OSO_3^-$.

24. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1, et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène, et où les dérivés précités conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés ou des dérivés de composés de la formule générale R_{fs}-$CH_2CH_2OC(O)CH_2CH_2N^+(H)[C_3H_6SO_3^-]C_2H_4N^+(CH_3)$ et de composés de la formule générale R_{fb}-$CH_2CH_2OC(O)CH_2$-$CH_2N^+(H)[C_3H_6SO_3^-]C_2H_4N^+(CH_3)$.

25. Composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1, et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène, et où les dérivés précités conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle le mélange de dérivés précité comprend des composés ou des dérivés de composés de la formule générale R_{fs}-$CH{=}CH_2$ et de composés de la formule générale R_{fb}-$CH{=}CH_2$ et leurs polymères.

26. Composition polymère comprenant un mélange de polymères comprenant des unités interpolymérisées dérivées d'un mélange de composés dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1, et dans laquelle les dérivés susdits conservent au moins 2 atomes de carbone du groupe de liaison d'alkylène, et où les dérivés précités conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée, dans laquelle les polymères précités comprennent une chaîne polymérique avec une pluralité de groupes perfluoroalkyle saturés pendants dans lesquels 50 à 95 % de ces groupes perfluoroalkyle sont droits et tous les autres groupes perfluoroalkyle sont ramifiés, et dans laquelle les groupes perfluoroalkyle sont directement liés à la chaîne de polymère ou sont liés à un atome de carbone d'alkylène.

27. Composition polymère suivant la revendication 26, dans laquelle le mélange de polymères précité comprend des homopolymères ou copolymères de polyacrylate.

28. Procédé de modification des propriétés superficielles d'un substrat, qui comprend la mise en contact de la surface dudit substrat avec la composition polymère suivant l'une ou l'autre des revendications 26 ou 27.

29. Procédé de modification de la tension superficielle ou de la tension interfaciale d'un corps de liquide, qui comprend l'addition à celui-ci d'une quantité d'une composition fluorochimique suffisante pour obtenir la tension superficielle ou tension interfaciale modifiée désirée dudit liquide, dans lequel la composition fluorochimique précitée comprend un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1 et dans laquelle lesdits dérivés conservent au moins deux atomes de carbone du groupe de liaison d'alkylène et où les dérivés susdits conservent le groupe perfluoroalkyle dans lequel

dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée.

30. Procédé de modification des propriétés superficielles d'un substrat, qui comprend la mise en contact de la surface dudit substrat avec une composition comprenant une composition fluorochimique, dans lequel la composition fluorochimique comprend un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1 et dans laquelle les dérivés susdits conservent au moins deux atomes de carbone du groupe de liaison d'alkylène et où ces dérivés conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée.

31. Substrat dont une surface est modifiée par une composition fluorochimique, dans lequel ladite composition fluorochimique comprend un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1 et dans laquelle les dérivés susdits conservent au moins deux atomes de carbone du groupe de liaison d'alkylène et où ces dérivés conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée.

32. Substrat suivant la revendication 31, dans lequel ledit substrat comprend une matière textile, du papier ou du cuir.

33. Corps de liquide comprenant une composition fluorochimique, ladite composition fluorochimique comprenant un mélange de composés, dans laquelle lesdits composés sont des dérivés d'un mélange précurseur comprenant les compositions de la revendication 1 et dans laquelle les dérivés susdits conservent au moins deux atomes de carbone du groupe de liaison d'alkylène et où ces dérivés conservent le groupe perfluoroalkyle dans lequel dans 50 à 95 % de ces dérivés le groupe perfluoroalkyle est à chaîne droite et dans tous les autres dérivés le groupe perfluoroalkyle est à chaîne ramifiée.

34. Procédé de préparation de la composition fluorochimique de la revendication 1, comprenant la réaction d'éthylène avec un mélange précurseur d'iodures de perfluoroalkyle ou de chlorures de perfluoroalkyl sulfonyle ou de bromures de perfluoroalkyl sulfonyle, dans lequel dans de 50 à 95 % de ces précurseurs le perfluoroalkyle est à chaîne droite et dans tous les autres précurseurs ce perfluoroalkyle est à chaîne ramifiée.

35. Procédé la revendication 34, dans lequel on prépare le mélange précurseur par fluoration électrochimique de l'analogue hydrocarboné.